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Organic Chemistry.

Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. III. Action of Ozone on *n*-Hexane. E. W. Blair, T. S. Wheeler, and W. Ledbury (*J. Soc. Chem. Ind.*, 1924, **43**, 287—289T).—The action of ozone on boiling *n*-hexane yields formaldehyde, acetaldehyde, and other aldehydes up to *n*-hexaldehyde; acids up to *n*-hexoic acid (produced in greatest quantity); also traces of carbon monoxide and dioxide and water. *n*-Hexyl *n*-hexoate and other esters are also formed.

Action of Bromine on *n*-Hexane. E. W. Blair, W. Ledbury, and T. S. Wheeler (*J. Soc. Chem. Ind.*, 1924, **43**, 289—290T).—*p*-Dibromobenzene and *trans*-benzene hexabromide are produced when nitrogen carrying the vapour of either benzene or *n*-hexane is passed through bromine at the ordinary temperature. It is probable that the hexane is converted into *cyclo*hexane and then into benzene by oxidation.

Liberation of Hydrogen from Carbon Compounds. I. Interaction of Acetylene, Methyl Alcohol, and Formaldehyde with Fused Alkali Hydroxides. H. S. Fry, E. L. Schulze, and H. Weitkamp (*J. Amer. Chem. Soc.*, 1924, **46**, 2268—2275).—The reaction between dry acetylene and an equimolecular mixture of sodium and potassium hydroxides at 300—325° yields various quantities of orthocarbonates, but no acetates as reported by Feuchter (A., 1914, i, 406). The quantity of carbonate produced is approximately proportional to the amount of acetylene introduced into the alkali hydroxides, but owing to decomposition of the acetylene, evidenced by deposition of free carbon, the amounts of hydrogen and methane are not in accord with the equation $C_2H_2+4NaOH \longrightarrow H_2+CH_4+C(ONa)_4$. Minute traces of unsaturated hydrocarbons are also formed. Similarly, methyl alcohol yields a mixture of carbonates and hydrogen, the ratios of the amounts of methyl alcohol consumed and carbon dioxide and hydrogen produced being in agreement with the equation $MeOH+2NaOH \longrightarrow Na_2CO_3+3H_2$. Formaldehyde behaves similarly, the ratio of the amounts of aldehyde consumed and carbon dioxide and hydrogen produced according approximately with the equation $CH_2O+2NaOH \longrightarrow Na_2CO_3+2H_2$. The reactions are in accordance with the general type reaction, $R(H)_n+nMOH \longrightarrow R(OM)_n+nH_2$, and are analogous to the reactions between glycol and potassium hydroxide and resorcinol and sodium hydroxide. The mechanism of the reactions is suggested by the

scheme $HC{:}CH+2NaOH \longrightarrow CHMe(ONa)_2$; $CHMe(ONa)_2+NaOH \longrightarrow CMe(ONa)_3+H_2$; $CMe(ONa)_3+NaOH \longrightarrow CH_4+C(ONa)_4$ (cf. Peters, this vol., ii, 174). The oxidation of cellulose by fused alkali hydroxides, yielding oxalates, conforms to the proposed type reaction. R. B.

Metallic Acetylides. II. Action of Acetylene on Metals. J. F. DURAND (*Bull. Soc. chim.*, 1924, [iv], **35**, 1141—1144; cf. this vol., i, 602).—By the direct action of acetylene on the metal at 450—500° (cf. Novak, A., 1909, i, 865; 1910, ii, 778) the author has obtained *beryllium acetylide*, *cadmium acetylide*, and a new *aluminium acetylide*, probably BeC_2, CdC_2, and $Al_2(C_2)_3$, respectively, and the zinc acetylide, ZnC_2, previously described (A., 1923, i, 449). These acetylides, which have not been obtained free from carbon or excess of the metal, are distinguished from magnesium acetylide in not giving rise to allylene derivatives; on treatment with water or dilute hydrochloric acid, acetylene is the only hydrocarbon produced, except in the case of aluminium acetylide when some methane is probably also formed (cf. Kusnetzoff, A., 1907, i, 669). Gold, palladium, uranium, and mercury give no acetylide under these conditions, and no acetylene could be obtained from the deposited carbon. The action of acetylene on aluminium and lead amalgams etc., and of iron, lead, etc. on acetylene in acetone solution, gave inconclusive results. R. B.

Comparison of Molecular Volume Numbers. R. LORENZ and W. HERZ.—(See ii, 823.)

Chlorination of Chloroform. H. GAULT and R. TRUFFAULT (*Compt. rend.*, 1924, **179**, 467—469).—Chlorine is without action on chloroform in the dark or when exposed to red or yellow light, but light of shorter wave-length favours the reaction, the velocity of which is most marked in the ultra-violet region. Dry chlorides of calcium, zinc, or aluminium act in some degree as catalysts, but ferric chloride appears totally to inhibit the reaction. This is due to its absorption of the radiations of effective wave-length, as no chlorinating action occurs when a screen of ferric chloride solution is interposed. When in very dilute solution, absorption of the activating radiation is incomplete and a small yield of carbon tetrachloride is obtained. The velocity of the reaction increases with temperature. H. J. E.

Organic Reactions at the Surfaces of Dehydrogenating Catalysts. H. ADKINS and W. A. LAZIER (*J. Amer. Chem. Soc.*, 1924, **46**, 2291—2305; cf. this vol., ii, 159).—The behaviour of ethyl alcohol, ethyl acetate, acetal, ether, acetaldehyde, and acetic acid at the surfaces of various catalysts containing nickel, copper, iron, and zinc has been investigated with a view to determine whether the reactions taking place are dependent on the physical nature of the surface or are characteristic of the metal present. Two distinct types of nickel are produced through reduction by

alcohol at 350—420° and by hydrogen at 300—400°. The former is at least twice as active as the latter in dehydrogenating alcohol and much more active in breaking down acetaldehyde to carbon monoxide and methane, practically no acetaldehyde being obtained from ethyl alcohol with this catalyst. In the hydrogenation of ethylene, it is only slightly superior, but with pure acetaldehyde, ethyl ether, and acetal it is many times as effective as nickel prepared with hydrogen. Neither catalyst is effective with ethyl acetate, whilst a catalyst reduced from nickel oxide by ethyl acetate itself is effective both against the ester and the alcohol; these facts, with the observations that nickel reduced with ethyl ether or acetal is reactive towards these compounds, whereas nickel reduced with hydrogen is not, lend some support to Boswell's theory of the activity of nickel catalysts. The evidence that oxygen must be present at a nickel surface in order that the nickel may function as a catalyst is inconclusive. If a nickel catalyst reduced by hydrogen is treated with oxygen, its activity towards dehydrogenation or decomposition is much increased, but this reactivation is not due to the addition of oxygen. Treatment of a hydrogen-reduced catalyst with oxygen followed by reduction with an organic reducing agent produces a much more effective catalyst than the original, the new catalyst producing a different proportion of reactions. A nickel catalyst reduced with alcohol does not lose its activity on treatment with hydrogen. The results obtained by passing a mixture of ethyl alcohol and acetic acid over nickel catalysts are in harmony with the activities when the two substances are reduced alone, the decomposition of ethyl alcohol being the more rapid reaction. The reactions under consideration are not successive reactions, the proportion of reaction products being determined by the nature of the catalyst, whilst the amount of reaction is dependent on variable factors such as time and temperature. The evidence indicates that the true catalyst is not a nickel oxide, but metallic nickel, and that the spacing of the active points is of fundamental importance, as it is in the case of non-reducible oxide catalysts. All nickel catalysts are characterised by their power of breaking carbon linkings, and this may be connected with the ability of nickel to pull electrons from their normal position between atoms.

When alcohol is passed over iron oxide obtained by drying precipitated ferric hydroxide or by igniting the nitrate or oxalate, the reactions involving the formation of methane and ethane and those of dehydrogenation occur in the proportion of 1 : 4 or 1 : 5. Iron oxide obtained from *methyl* or *ethyl ferrite*, however, behaved like reduced iron, yielding almost entirely a straight dehydrogenation to acetaldehyde and hydrogen. Copper catalysts obtained by ignition of copper nitrate, oxalate, and formate and by reduction of cuprous oxide give a similar straight dehydrogenation of ethyl alcohol. Zinc oxide obtained from zinc hydroxide dehydrogenates six times as much alcohol as it dehydrates, whilst with zinc oxide from *zinc* iso*propoxide*, the ratio dehydrogenation/dehydration is only 4/1, and in the latter case 5—6% of carbon dioxide is produced,

whereas in the first case only 1—2% is formed. The catalyst from *zinc butoxide* is intermediate between these two catalysts. The oxide obtained from the *iso*propoxide gives results with acetaldehyde almost identical with those from iron oxide in the proportions of the reaction products, whereas the catalyst from zinc hydroxide gives 25% less carbon dioxide, 30% more carbon monoxide, and 40% less hydrogen. Generally, the catalyst from zinc *iso*propoxide is much the more active. The cases of zinc and ferric oxides are thus similar to alumina and titania in that the relative activities of the catalysts for different simultaneous reactions on their surfaces are determined by the solid compound which is converted into the catalyst, in contrast to nickel catalysts, the relative activity of which is determined by the process by which the nickel compound is reduced (cf. Kelber, this vol., ii, 244). The experimental results of Sabatier and Mailhe are criticised as inconclusive owing to their nickel having been partly reduced by hydrogen and partly by alcohol. R. B.

Catalytic Dehydration of Alcohol and Ether by Alumina. J. B. SENDERENS (*Bull. Soc. chim.*, 1924, [iv], **35**, 1144—1145).—The results obtained by Pease and Young (this vol., i, 363) have already been described by the author (A., 1909, i, 127; 1912, i, 406). R. B.

Odour and Chemical Constitution. A. MÜLLER (*Deuts. Parfümerie Ztg.*, 1923, **9**, 5—6; from *Chem. Zentr.*, 1924, i, 2778).—The *dimethyloctanols* prepared by reducing active citronellal and inactive citral with nickel and hydrogen have different odours, the alcohol from citronellal smelling like *iso*pulegol. Carefully purified inactive dimethylnonanol had a cruder and more intense odour than the active alcohol. F. A. M.

Density of Gaseous Dimethyl Ether. T. BATUECAS (*Compt. rend.*, 1924, **179**, 440—443).—The mean value of a series of twenty determinations of the weight of a litre of gaseous dimethyl ether under standard conditions is 2·1097 g. This is in agreement with the value obtained by Baume (A., 1908, ii, 372). The gas used was prepared by two different methods. H. J. E.

Velocity of Hydrolysis of Ethyl Ether. A. SKRABAL and H. AIROLDI.—(See ii, 842.)

Action of Chlorine on Trimethylene Trisulphide. J. GIRON (*Bull. Sci. Pharmacol.*, 1924, **31**, 25—27; from *Chem. Zentr.*, 1924, i, 2774).—On passing a stream of chlorine over methylene sulphide and fractionating the product, a substance, (?) $CH_2Cl{\cdot}S{\cdot}CHCl_2$, b. p. 85—86°/29 mm., d_4^{24} 1·6374, is obtained. F. A. M.

Ionisation of Some Organic Acids dissolved in Mixtures of Water and Ethyl Alcohol. M. DUBOUX and D. TSAMADOS.—(See ii, 827.)

Preparation of β-Chloropropionic Acid. C. Moureu and R. Chaux (*Bull. Soc. chim.*, 1924, [iv], **35**, 1360—1364; cf. A., 1917, i, 534; 1921, i, 495; 1922, i, 105).—Dry hydrogen chloride is passed into acraldehyde at −15° until the theoretical gain in weight has taken place. The product is then oxidised in small quantities at a time by adding it slowly, with agitation, to fuming nitric acid (*d* 1·49). At first, the temperature is kept between 30° and 35°, but the action is completed on the water-bath. The yield of β-chloropropionic acid averages 65%, but with specially pure nitric acid it may reach 70%. W. E. E.

Optically Active αβ-Dibromopropionic and αβ-Dichloropropionic Acids. P. Karrer and W. Klarer (*Helv. Chim. Acta*, 1924, **7**, 929—931).—By the action of cold nitrosyl bromide *d*-αβ-diaminopropionic acid is converted into d-αβ-*dibromopropionic acid*, b. p. 129°/9 mm., m. p. 64—66°, $[\alpha]_D^{20}$ +6·5° to +7·0° in water. In the same way, nitrosyl chloride gives d-αβ-*dichloropropionic acid*, b. p. 113°/12 mm., m. p. 36°, $[\alpha]_D^{20}$ +18·8°. In both cases, it is possible that racemisation has taken place. *d*-αβ-Dibromopropionic is transformed into *l*-glyceric acid. W. E. E.

Autoxidation of Crotonaldehyde. Preparation of Crotonic Acid. A. Duchesne and M. Delépine (*Bull. Soc. chim.*, 1924, [iv], **35**, 1311—1317).—Oxygen is bubbled through three flasks of crotonaldehyde connected in series; the first two flasks are maintained at 70°. After the third or fourth day, the first flask is removed and its place taken by the second; the third flask takes the second place and a fresh flask of aldehyde is connected at the end. Besides crotonic acid (yield 45—50%), acetic acid and a resin are formed. In small quantities, ferric oxide and manganese hydroxide accelerate the oxidation, but foreign acids are still produced and the yield is little improved. Dilution of the crotonaldehyde with ether or benzene reduces the yield of acid obtainable; the presence of alcohol, water, or light petroleum (b. p. 100°) in sufficient quantity prevents oxidation altogether. W. E. E.

Fish Oils. Quantitative Analysis of Sardine Blubber. A. Eibner and E. Semmelbauer (*Chem. Umschau*, 1924, **31**, 189—197; 201—209).—A sample of sardine blubber, forming a viscous, brownish-yellow oil which deposited crystalline fats at ordinary temperatures, had the following constants: iodine value, 136·0; acid value, 18·8; ester value, 179·8; saponification value, 194·9; unsaponifiable matter, 0·5%; ash, 0·18%. It contained clupanodonic acid, 12·7%; α-linoleic acid, 9·8%; *iso*linoleic acid, 10·1%; oleic acid, 28·6%; hydroxy-acids, 8·7%; saturated acids, 22·0%; glycerol, 4·1%; and cholesterol, 0·5%. Tsujimoto's formula for clupanodonic acid (A., 1923, i, 297) was confirmed, and the presence in the blubber of dipalmitostearin, oleodipalmitin, and probably the triglyceride of clupanodonic acid was established. [Cf. *B.*, 1924, 986.] F. G. W.

Velocity of Hydrolysis of Ethyl Orthoacetate. A. SKRABAL and M. BALTADSCHIEWA.—(See ii, 842.)

Mutual Relationship of the Formation of Oxalic and Citric Acids with Different Species of *Aspergillus niger*. C. WEHMER (*Ber.*, 1924, **57**, [*B*], 1659—1665).—The action of various species of *Aspergillus niger* on sugar solutions in the presence of potassium nitrate, potassium dihydrogen phosphate, magnesium sulphate, and calcium carbonate leads to the production of calcium oxalate and, frequently, of calcium citrate. The formation of calcium citrate is particularly noticeable when potassium nitrate is replaced by ammonium nitrate as source of nitrogen. The hypothesis that the production of oxalic acid from sucrose occurs through the intermediate formation of calcium hydrogen citrate is supported by the observation that oxalic acid is freely produced by the action of *A. niger* on solutions of sodium, ammonium, or calcium hydrogen citrates in which these salts are the sole source of carbon; normal calcium citrate does not undergo a similar change. With certain species of *Aspergillus*, notably *A. niger japonicus*, production of oxalic acid does not occur. Calcium hydrogen citrate is converted by this mould into the normal citrate, the citric acid appearing to be transformed directly into carbon dioxide; it is noticeable that the salt is never decomposed completely. Cessation of activity is attributed to the diminishing acidity of the solution; with moulds which yield oxalic acid, such diminution does not occur, since the utilised citric acid is replaced by oxalic acid. H. W.

Glutaconic Acids. XVII. Tendency towards Reversion to Type. C. K. INGOLD, J. H. OLIVER, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 2128—2136).—When mobile derivatives of the glutaconic acids are transformed into static derivatives, the latter exhibit a remarkable instability and tendency to revert to a mobile form. The reversion of static dibromo-additive products into glutaconic acids is believed to take the following course, $CO_2H{\cdot}CH_2{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH{:}CBr{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$, since intermediate compounds have been isolated. By exposure of ethyl aconitate to bromine vapour for 2—3 weeks, it is converted into ethyl αβ-dibromotricarballylate, which on distillation yields the *lactone* ester of *bromohydroxytricarballylic acid*, b. p. 205°/10 mm., and on hydrolysis with barium hydroxide, sodium carbonate, or methyl-alcoholic potassium hydroxide gives aconitic acid. When treated with cold alcoholic sodium ethoxide, the ethyl dibromo-ester yields ethyl α-bromoaconitate, which on hydrolysis gives rise to aconitic acid.

The tendency of the dibromides to regenerate the parent acids depends on the mobility of the acids produced. Glutaconic acid itself is the most mobile and can only be isolated in one form, and the labile form of the ester has a very transitory existence. Introduction of substituents in either the α- or β-positions decreases the mobility. Thus the normal form of α-methylglutaconic acid was converted into *αβ-dibromo-α(or -γ)-methylglutaric acid*, m. p.

178° (decomp.), by the action of bromine vapour; the acid yields normal α-methylglutaconic acid when hydrolysed. Similarly, normal β-methylglutaconic acid was transformed into *αβ-dibromo-β-methylglutaconic acid*, m. p. 142°, from which only the labile form of β-methylglutaconic acid is obtained by hydrolysis.

The tendency to reduction is suppressed by introducing two substituents, either in the αβ- or αγ-positions. αβ-Dimethylglutaconic acid, when exposed to bromine vapour, yields *α-bromo-αβ(or -βγ)-dimethylglutaric acid*, m. p. 115° (decomp.), whereas the corresponding αγ-dimethylglutaconic acid gives αβ-dibromo-αγ-dimethylglutaric acid, m. p. 134°; both bromo-acids are converted by the action of alkalis into hydroxylation products, and not into glutaconic acids.

The reaction is confined to glutaconic acids and is not shown by static unsaturated acids of the αβ- and βγ-type. Thus, vinylacetic acid can be converted into crotonic acid and *cyclo*hexylideneacetic acid into *cyclo*hexeneacetic acid, but when their dibromides are treated with dilute alkalis the unsaturated acids are not regenerated.

In all these cases, the replacement of the halogen by hydrogen in presence of aqueous alkali hydroxide results in the formation of alkali hypobromite in solution. Reduction was carried out in alcoholic solution of sodium ethoxide. Under these conditions, ethyl bromoaconitate might yield ethyl ethylaconitate and sodium hypobromite or ethyl aconitate and ethyl hypobromite. That the latter course is the more probable has been shown by conducting an experiment in presence of ethyl malonate, which by oxidation consequent on reduction of the bromoaconitate gives ethyl ethanetetracarboxylate. C. J. S.

Metallic Hydroxy-acid Complexes. III. Constitution of Cuprimalates and Analogous Compounds. I. W. WARK (*J. Chem. Soc.*, 1924, **125**, 2004—2009).—The isomeric change from cupric malate to cuprimalic acid is regarded as merely due to the wandering of a hydrogen atom resulting in a structure in which the copper atom replaces one atom of hydrogen in an alcoholic hydroxyl group and one atom in a carboxyl group. This idea is extended to the structure of certain alkaline complexes containing copper. In disagreement with the view of Pickering, the constitution of potassium cupricitrate, $(C_6H_4O_7)_2K_6Cu,6H_2O$, is considered to be $(CO_2K\cdot CH_2)_2\overset{b}{C}(OK)\cdot CO\cdot O\cdot Cu\cdot O\cdot C(CH_2\cdot CO_2K)_2\cdot CO_2K$, in which the potassium atom *b* imparts alkalinity to the compound. Similarly, to the alkaline cupriglycollate described by Pickering (T., 1911, **99**, 1347) is assigned the structure

$$OK\cdot CH_2\cdot CO\cdot O\cdot Cu\cdot O\cdot CH_2\cdot CO_2K,2H_2O.$$

The alkali derivatives of tartaric acid of the type $M_2CuC_4H_2O_6$, obtained by Bullnheimer and Seitz, have the structure

$$CO_2M\cdot CH(OM)\cdot CH<\begin{matrix}CO\cdot O\\ |\\ O-Cu\end{matrix}.$$

A second type of complex, in which the copper atom replaces the hydrogen atom in two hydroxyl groups, is exemplified in the

derivatives of monobasic monohydroxy-acids such as lactic and salicylic acids. C. J. S.

Rotatory Dispersion of Tartaric Acid. T. M. LOWRY and P. C. AUSTIN.—(See ii, 714.)

Condensation of Acetoacetic Esters with Malonic Esters. H. GAULT and H. KLEES (*Compt. rend.*, 1924, **179**, 600—601).—A preliminary note. Ethyl α-chloroacetoacetate and ethyl sodiomalonate do not interact until heated; then, after several hours on the steam-bath, ethyl acetate and ethyl ethane-ααβ-tricarboxylate are formed. Reaction takes place with ethyl α-bromoacetoacetate in the cold; the oily product contains a little (1—3%) ethyl ethane-ααβ-tricarboxylate, ethyl malonate (53%), and ethyl diacetylfumarate (?), m. p. 123°. Ethyl sodioacetoacetate and ethyl bromomalonate yield a little ethyl malonate and ethyl ethanetetracarboxylate, together with a *liquid*, b. p. 224—230°/10 mm., in the formation of which 2 mols. of ethyl acetoacetate and 1 mol. of ethyl malonate have taken part. W. A. S.

Biological Oxidation. III. The Oxide of the SH-Group and Oxidation by Means of Ethyl Peroxide. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **149**, 188—190).—Using a new preparation of thioglycollic acid the author has been unable to repeat his previous observations (this vol., i, 708) regarding the structure of the intermediate oxide formed by the acid, and the further possibility of the intermediate compound being a hydroperoxide is also dismissed. Ethyl peroxide in the presence of iron and oxygen at 37° oxidises α-hydroxy-acids, formic, acetic, and glycerophosphoric acids, whilst mono- and di-hydric alcohols, aldehydes, glycerol, acetone, mono- and di-carboxylic acids, and β-hydroxy-acids are not oxidised. J. P.

Functional Derivatives of α-Sulphobutyric Acid and the Rotatory Power of their Active Components. H. J. BACKER and J. H. DE BOER (*Rec. trav. chim.*, 1924, **43**, 420—433; cf. this vol., i, 708; also Backer, A., 1921, i, 855).—*Aniline butyranilide-α-sulphonate*, m. p. 253—256°, obtained by the action of excess of aniline on aniline sulphobutyrate, reacts with barium hydroxide or carbonate, yielding *barium butyranilide-α-sulphonate*. The latter, when treated with copper, cobalt, or nickel sulphate, yields the corresponding metallic *salt* of the butyranilide-sulphonic acid. p-*Toluidine butyro*-p-*toluidide-α-sulphonate*, m. p. 245—250°, p-*anisidine butyro*-p-*anisidide-α-sulphonate*, m. p. 242°, and p-*phenetidine butyro*-p-*phenetidide-α-sulphonate*, m. p. 261—262°, were prepared by heating the corresponding acid sulphobutyrate with excess of the base already present. On heating *o*-phenylenediamine sulphobutyrate, *benziminazole-2-propylsulphonic acid* is formed, of which the *barium* and *cobalt* salts are described. 3 : 4-Diaminotoluene sulphobutyrate similarly yields *methylbenziminazole-2-propylsulphonic acid*. Resolution of butyranilide-α-sulphonic and benziminazole-2-propylsulphonic acids into their optical isomerides was effected by means of their *strychnine* salts; in addition, the

active *barium*, *copper*, *cobalt*, and *nickel* salts of the former acid and the *barium* and *cobalt* salts of the latter were obtained. Variation in molecular rotation with wave-length is shown diagrammatically for both aqueous and alcoholic solutions of copper and cobalt butyranilide-α-sulphonate; the curves exhibit some marked abnormalities. H. J. E.

Preparation of Acetone from Acetic Acid. I. M. MASHINO (*J. Chem. Ind. Japan*, 1924, **27**, 804—809).—Acetone is obtained when a mixture of acetic acid vapour and nitrogen is passed over heated granulated calcium oxide at 260—550°. The optimum temperature is 400—500°. The yield (about 54%) of acetone is best when acetic acid is passed at the rate of 7—10 g. per hour at 450°, but is only slightly decreased by passing the acid at the rate of 16 g. per hour at 550°. K. K.

Catalytic Reduction of Oximes in the Presence of Colloidal Palladium. W. GULEWITSCH [with B. SSEMENOWITSCH, S. KAPLANSKY, and L. BRONDE] (*Ber.*, 1924, **57**, [*B*], 1645—1653).—Ethyl β-aminobutyrate is not formed by the catalytic hydrogenation of ethyl β-oximinobutyrate in aqueous-alcoholic solution in the presence of colloidal palladium; the observed absorption of hydrogen is due to fission of the oxime and reduction of the liberated hydroxylamine to ammonia. Acetoxime and methyl ethyl ketoxime could not be reduced under similar conditions, although the potential activity of the catalyst remained unaltered. Benzaldoxime, on the other hand, yields a mixture of mono- and di-benzylamine, ammonia, and benzaldehyde (cf. Paal and Gerum, A., 1909, i, 381; Rosenmund and Pfankuch, this vol., i, 34); dibenzylamine is readily characterised by its *nitrate*, m. p. 194°. Benzophenoneoxime gives diphenylmethylamine, but acetophenoneoxime and dibenzylketoxime could not be reduced. Acetaldoxime and propaldoxime are reduced exclusively to the corresponding tertiary amines. Reduction takes place only at the commencement of the experiment; subsequently, when the reaction appears to proceed more slowly, the oxime probably becomes hydrolysed and the liberated hydroxylamine is converted into ammonia. The production of the tertiary amine is not due to elimination of ammonia from preformed, primary amine. H. W.

Diacetone [Di-*iso*propylidene] Compounds of Arabinose and Galactose. O. SVANBERG and S. W. BERGMAN (*Arkiv Kemi, Min., Geol.*, 1924, **9**, 1—16).—The monoacetone derivatives of arabinose and galactose are not formed by hydrolysis of the diacetone compounds. The action of sulphuric acid on an acetone solution of arabinose yields diacetonearabinose [arabinose di*iso*propylidene ether] (yield 92—93%), m. p. 41—42°, b. p. 85—87°/1 mm., 90—91°/2 mm., $[\alpha]^{18}_{\text{Hg yellow}}$ +5·5°±0·2 in water (cf. Fischer, A., 1895, i, 437), which is quantitatively hydrolysed by 0·5% hydrochloric acid (but not by 0·1—0·2% acid) to arabinose. It was found that α-galactose was not acted on by acetone and sulphuric acid, but β-galactose dissolved, and was converted into its di*iso*-

propylidene derivative, b. p. 126°/1 mm., $[\alpha]^{18}_{Hg\ yellow}$ −46° in water (cf. Freudenberg and Hixon, A., 1923, i, 1179). On hydrolysis, it behaved like diacetonearabinose. Diacetonegalactose on oxidation with potassium permanganate gave a positive, but diacetoneglucose a negative phloroglucinol test; it may be concluded that in the former case the OH in position 6 is unsubstituted, so that oxidation to a glycuronic acid derivative occurs (cf. Karrer and Hurwitz, A., 1921, i, 767; Irvine and Patterson, T., 1922, **121**, 2146). F. M. H.

Examination of Photosynthetic Sugars by the Methylation Method. J. C. Irvine and G. V. Francis (*Ind. Eng. Chem.*, 1924, **16**, 1019—1020).—A sample of syrup prepared by photosynthesis from formaldehyde was found to contain no polysaccharides of the type, $C_6H_{10}O_5$, or ketoses, but to have an apparent methoxyl content of 9—12%. Part of the reducing power to Fehling's solution was due to substances other than sugars. The syrup was purified by drying at 80° under a pressure of 0·2 mm. of mercury and was then subjected to methylation, whereby a fraction was obtained with a methoxyl content of 54·5% and a molecular weight of 232. After hydrolysis, the composition of the product closely corresponded with tetramethylhexose. It is deduced that the original proportion of hexoside present could not exceed 10%. The bulk of the syrup (to the extent of at least 80%) consists of non-sugar compounds which contain hydroxyl groups. C. I.

The Glucose of Sucrose. H. Colin and A. Chaudun (*Bull. Soc. Chim. biol.*, 1924, **6**, 625—630).—Polarimetric measurements show that the dextrose produced in the inversion of sucrose has at first a higher rotatory power than ordinary dextrose, but rapidly attains the normal value; it is therefore probably first split off from the sucrose molecule as α-glucose. C. R. H.

Preparation of β-Methylglucoside. H. H. Schlubach and K. Maurer (*Ber.*, 1924, **57**, [*B*], 1686—1687).—β-Methylglucoside is the primary product of the methylation of dextrose by Haworth's method (T., 1915, **107**, 8), but its isolation from the product of the reaction is rendered difficult by the presence of sodium methyl sulphate. Separation may be readily effected if the dry product is acetylated with acetic anhydride and pyridine and the mixture poured into ice-water. Sodium methyl sulphate passes into solution, whereas tetra-acetyl-β-methylglucoside is precipitated in the homogeneous condition and is subsequently hydrolysed to β-methylglucoside, the yield being about 40%. H. W.

Inversion of Sucrose and Determination of Hydrion Concentration. M. Duboux.—(See ii, 842.)

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acid in presence of sodium chloride has been determined. The *E.M.F.* slowly falls to a constant value about 1% smaller than the initial value of the cadmium cells employed, and hence the apparent hydrogen-ion concentration increases by about 7% during the inversion. C. J. S.

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The usual method of following the inversion while the lag is present gives the correct value of k_1 if certain precautions are observed, but the curve $\log(\lambda_t-\lambda_\infty)$ with lag against time does not extrapolate to $\log(\lambda_0-\lambda_\infty)$ at $t=0$, but to $\log\{\lambda_0-\lambda_\infty+A(R+S)\}$, where $R+S$ is the total lag constant under the given conditions, k_1 being given by $1/t\log[\lambda_0-\lambda_\infty+A(R+S)]/(\lambda_t-\lambda_\infty)$. The short-interval formula also gives the correct value of k_1 (whether the lag is appreciable or not), provided it is not applied at the initial stages of the inversion. C. J. S.

Action of Ultra-violet Radiations on Solutions of Sucrose. P. BEYERSDORFER and W. HESS (*Ber.*, 1924, **57**, [*B*], 1708—1711).—The photochemical decomposition of $M/8$, $M/2$, and $2M$ solutions of sucrose in water has been investigated at 20°, 70°, and 100°, the course of the change being followed by observations of the optical rotation, acidity, and reducing power of the solutions. Reaction is scarcely appreciable at 20°, but the rate increases first slowly and then rapidly with increasing temperature. The photochemical degradation of sucrose is almost completely inhibited by the presence of chlorophyll or, to a less extent, of green-PLX. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide have little influence on the change, which, however, scarcely occurs in the presence of sodium acetate; this result is not surprising, since the latter salt is known to prevent inversion of sucrose. The sucrose molecule is so stable towards the action of light of short wave-length that the union of its component parts by an oxygen atom appears improbable. On the other hand, lævulose is considerably more rapidly decomposed than dextrose. The products of the decomposition of sucrose are carbon monoxide, carbon dioxide, hydrogen, methane, organic acids, aldehydes, ketones, and alcohols, together with condensation products of the

propylidene derivative, b. p. 126°/1 mm., $[\alpha]^{18}_{Hg\ yellow}$ −46° in water (cf. Freudenberg and Hixon, A., 1923, i, 1179). On hydrolysis, it behaved like diacetonearabinose. Diacetonegalactose on oxidation with potassium permanganate gave a positive, but diacetoneglucose a negative phloroglucinol test; it may be concluded that in the former case the OH in position 6 is unsubstituted, so that oxidation to a glycuronic acid derivative occurs (cf. Karrer and Hurwitz, A., 1921, i, 767; Irvine and Patterson, T., 1922, **121**, 2146). F. M. H.

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type of dextrin and caramel. A crystal of sucrose when exposed to ultra-violet rays at 70° becomes coated on the exposed surface with a brown layer of caramel. The prolonged exposure of sucrose solutions to ultra-violet rays appears to yield sensibly the same products as are obtained by the dry distillation of sugar. H. W.

Variation of the Optical Activity of Sucrose on Heating. M. A. RAKUSIN and A. N. NESMEJANOV (*Z. Unter. Nahr. Genussm.*, 1924, **48**, 151—152).—Commercial sucrose, m. p. 178—183°, $[\alpha]_D$ +65·33°, was caramelised by heating first to a temperature above the melting point and then maintaining at a lower temperature for varying lengths of time. Experiments were carried out at 160° to 190° for periods up to 4 hours. In all cases decrease of the rotatory power was observed varying with the temperature and duration of the experiment. After heating at 180° for 30 mins., the sugar was rendered optically inactive; after 2 hours at 150° the rotatory power was $[\alpha]_D$ +13·2°, and after 4 hours at 140°, $[\alpha]_D$ +21·0°. G. S. W.

Trihexosan. A. PICTET and R. SALZMANN (*Helv. Chim. Acta*, 1924, **7**, 934—935).—The trihexosan obtained as the ultimate product of depolymerisation of starch by heat is hydrolysed by emulsin to dextrose and a dihexosan, m. p. 209—210° (decomp.), $[\alpha]_D$ +133·2°, which may be identical with the product of Pringsheim and Wolfsohn (this vol., i, 714). At present, it seems that the trihexosan is a β-glucosyldihexosan. W. E. E.

A Hexahexosan Obtained from Starch. A. PICTET and P. STRICKER (*Helv. Chim. Acta*, 1924, **7**, 932—933).—Potato starch is heated at 200° with glycerol (Pictet and Jahn, A., 1922, i, 987) until the red coloration given with iodine is at its brightest, whereby a *hexahexosan*, decomp. about 225°, is isolated as a white, amorphous powder; it does not reduce Fehling's solution. When heated with acetic anhydride and sodium acetate it gives the trihexosan nona-acetate described by Pictet and Jahn (*loc. cit.*). W. E. E.

Hydrolysis of Starch by Salts. III. Hydrolysis by Inorganic Catalysts (Artificial Oxydases). W. BIEDERMANN and C. JERNAKOV (*Biochem. Z.*, 1924, **149**, 309—328).—The hydrolysis of starch and the amyloses by salts of the heavy metals such as iron, copper, and manganese in the presence of hydrogen peroxide, and the typical "salt hydrolysis" shown by the chlorides and bromides of the alkali and alkaline-earth metals, suggest a parallelism between such hydrolytic actions and the oxydase- or peroxydase-like action of the salts towards guaiacum and other oxydase reagents. Manganese chloride may act on guaiacum and on starch in the absence of hydrogen peroxide and its action is therefore analogous to that of the alkali metals. J. P.

Polysaccharides. XXVIII. Reserve Cellulose (Lichenin). P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, **7**, 928—929).—Although one of the preparations examined contained only 0·0055%

of phosphorus, it is certain that lichenin contains that element; the small proportion may be due to the action of large amounts of boiling water used to purify the lichenin. The ash of lichenin amounted to 0·9—1%, and contained much calcium, a little magnesium and iron, and only traces of silicic acid. When lichenin is quickly distilled at 12 mm., *l*-glucosan is obtained. W. E. E.

Proposed Definition of "Cellulose." P. KLASON (*Papier-Fabr.*, 1924, **22**, 373—377).—Two reagents are proposed for the complete removal of lignin from wood under conditions such that the cellulose residue remains constant in weight even after excessively prolonged digestion. They are both made up with 80 g. of sodium hydrogen sulphite per litre, but the weaker one contains 200 c.c. and the stronger 500 c.c. of *N*-hydrochloric acid per litre. The wood is digested continuously at 98°, the liquor being siphoned off and renewed every 4 days, until the residue is substantially constant in weight and free from lignin. With the weaker acid, spruce wood in chips or rasped yields 54% of cellulose after 9—12 days' digestion, but with the stronger acid, the yield from rasped wood is about 7% lower, whereas that from chipped wood is only 1·5% lower. Hence it is suggested that spruce wood contains two types of cellulose, one resistant to the stronger acid and corresponding with crystalline cellulose and the other resistant only to the weaker acid and corresponding with amorphous cellulose. In the natural condition, the crystalline cellulose protects the amorphous, but when the cells are ruptured by rasping this protection ceases. The degree of protection of the less resistant cellulose by the more resistant varies according to the species, and this protection is less complete in beech wood than in spruce wood. Cotton cellulose also resists the weaker acid, but breaks down, yielding only 90·5% residue with the stronger acid. The use of the weaker acid under the above conditions is suggested as the basis of an analytical definition of "cellulose." [Cf. *B.*, 1924, 976.] J. F. B.

Preparation of Cellulose Acetates. A. CAILLE (*Chim. et Ind.*, 1924, **12**, 441—448).—A suitable mixture for the acetylation of 100 g. of cotton consists of 600 g. of 44·8% acetic anhydride with 15 g. of sulphuric acid. Avoiding rapid rises of temperature, the cotton goes smoothly into solution in about 6 hours with a maximum temperature of 38°. Higher temperatures yield products of low viscosity; smaller quantities of sulphuric acid involve prolonged periods of acetylation and inferior esterification. During the primary acetylation, the proportions of combined acetic and sulphuric acids increase steadily until the product, precipitated at the stage when the cotton fibre is entirely dissolved, contains 66—67% of acetic acid and 0·97% of sulphuric acid. These products are mixed acetic–sulphuric acid esters, and the secondary modification, induced by the introduction of 20 g. of water to the acetylated mixture, consists of an acid hydrolysis of the sulphuric acid ester. The stability of the ultimate cellulose acetate depends on the elimination, as completely as possible, of the combined sulphuric

acid groups. This may be promoted by a secondary hydrolysis of the precipitated solid by digestion with 0·25% sulphuric acid at 75°. The acid function of the sulphuric acid ester is capable of neutralisation by mineral bases yielding ester salts, so that products washed with calcareous water are far more stable than those washed with distilled water. J. F. B.

Constitution of the Anhydrides of Glutamic Acid. A. Blanchetière (*Bull. Soc. chim.*, 1924, [iv], **35**, 1317—1325).—The results of biuret tests on the tri*cyclo*peptide from glutamic acid (A., 1923, i, 12) are sometimes positive and sometimes negative. This is explained if the tri*cyclo*peptide gives rise to the two forms of glutamylglutamic acid,

I. $CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$,

II. $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$,

which are theoretically possible. Actually, when the tri*cyclo*peptide is hydrolysed with sodium or barium hydroxide, a crystalline glutamylglutamic acid is obtained together with a gum which is thought to be the second form of the acid. According to the results of the biuret reaction, the crystalline form has the structure I. W. E. E.

Formaldehyde Compounds of Simple Amino-acids. H. Krause (*Z. physiol. Chem.*, 1924, **139**, 216—218).—Polemical (cf. Krause, A., 1919, i, 67; Bergmann, Jacobsohn, and Schotte, this vol., i, 19). C. R. H.

Carbamide and Guanidine Derivatives of Aliphatic Sulphonic Acids. II. R. Andreasch (*Monatsh.*, 1924, **45**, 1—7).—The action of potassium sulphite on certain bromoacylcarbamides and on chloroacetamide is described.

In completion of earlier work (A., 1923, i, 546), the *barium* salt ($+2H_2O$) of sulphoacetylcarbamide is described. α-Bromopropionylcarbamide was converted by aqueous-alcoholic potassium sulphite into the *potassium* salt ($+1\frac{1}{2}H_2O$) of α-sulphopropionylcarbamide. Interaction of ethyl bromopropionate and thiocarbamide in alcoholic solution formed the *hydrobromide* of methylthiohydantoin. The corresponding hydrochloric acid solution was oxidised with potassium chlorate at 50—60° to the potassium salt of α-sulphopropionylcarbamide. Aqueous methylthiohydantoin hydrobromide treated with bromine at 60° followed by barium carbonate gives barium α-sulphopropionate, doubtless formed by hydrolysis of the expected sulphonate of propionylcarbamide. By heating phenylcarbamide with bromopropionyl bromide at 135—155°, *α-bromopropionylphenylcarbamide*, m. p. 162°, was obtained. Its interaction with potassium sulphite gave the *potassium* salt ($+H_2O$) of α-sulphopropionylphenylcarbamide. By heating α-bromo*iso*valeryl chloride and ethylcarbamide, there was obtained *α-bromoisovalerylethylcarbamide*, m. p. 110° (cf. D.R.-P. 185962). Potassium sulphite replaced the bromine by hydrogen, giving *ethylisovalerylcarbamide*, m. p. 120°. Similarly, α-bromo-α-ethylbutyrylcarbamide gave α-ethylbutyrylcarbamide, m. p. 206°.

With potassium sulphite, the halogen in halogen derivatives of acid amides is readily replaced by HSO_3. Thus chloroacetamide yields the *potassium* salt of sulphoacetamide. *Sodium* and *ammonium* salts are prepared analogously. F. M. H.

Derivatives of Methylstannonic Acid. II. H. Lambourne (*J. Chem. Soc.*, 1924, **125**, 2013—2015).—Penta-acyl derivatives of the type

$$SnMe(O{\cdot}COR)_2{\cdot}O{\cdot}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR)_2,$$

have been obtained by the action of dichloroacetic, propionic, *n*-butyric, and *iso*butyric acids on methylstannonic acid, R being $CHCl_2$, Et, Pr^{α}, or Pr^{β}, respectively. The *pentadichloroacetyl* compound has m. p. 235—240° (decomp.). The *pentapropionyl* compound melts at 156—157°, solidifies again at 160°, and remelts at about 240°. The *pentabutyryl* compound and *pentaisobutyryl* compound have m. p. 105° and 194°, respectively.

The propionyl, butyryl, and *iso*butyryl penta-acyl derivatives when hydrolysed with alcohol yield hexa-acyl derivatives, regarded as having a cyclic structure.

The *hexapropionyl* compound partly melts at about 246° (decomp.), and is completely hydrolysed to methylstannonic acid on repeated boiling with alcohol. The *hexabutyryl* and *hexaisobutyryl* compounds have m. p. 180° and about 260°, respectively.

C. J. S.

Magnesium Acetylenyl Bromide. J. Salkind and A. Rosenfeld (*Ber.*, 1924, **57**, [*B*], 1690—1692).—Magnesium acetylenyl bromide, CH:C·MgBr, is almost the sole product of the action of acetylene on magnesium and bromobenzene in the presence of ether if the boiling solution is continuously saturated with the gas during the whole course of the reaction. It is converted by acetophenone into *γ-phenyl-Δ$^{\alpha}$-butinen-γ-ol*,

$$CMePh(OH){\cdot}C{:}CH,$$

an almost colourless liquid which cannot be distilled (the *copper* derivative is described) together with smaller amounts of the βε-diphenyl-Δ$^{\gamma}$-hexinene-βε-diols. H. W.

Stereoisomeric Forms of Decahydronaphthalene (Decalene). F. Eisenlohr and R. Polenske (*Ber.*, 1924, **57**, [*B*], 1639—1644).—*cis*-Decahydronaphthalene, b. p. 193°/768 mm., $d_4^{20\ vac.}$ 0·8953, n_{α}^{20} 1·47817, is prepared by the action of a solution of sodium in absolute alcohol at 200° on *cis*-β-decahydronaphthalenesemicarbazone, m. p. 183°. Particularly if the alcohol used contains a trace of water, the hydrocarbon is accompanied by a considerable proportion of *cis*-decahydro-β-naphthol, which is transformed by potassium hydrogen sulphate at 200° into *cis*-octahydronaphthalene, b. p. 194°/771 mm., $d_4^{20\ vac.}$ 0·9090, n_{α}^{20} 1·49124. The unsaturated hydrocarbon is smoothly hydrogenated in ethereal solution in the presence of spongy platinum to *cis*-decahydronaphthalene, the physical constants of which agree with those of the product described above. *trans*-β-Decahydronaphthalonesemi-

carbazone (cf. Häckel, this vol., i, 32) is converted similarly by sodium ethoxide solution at 210° into a mixture of *trans*-decahydro-β-naphthol and *trans*-decahydronaphthalene, b.p. 185°/756 mm., $d_4^{20\ vac.}$ 0·8823, n_α^{20} 1·47218. The hydrocarbon having almost identical physical constants is also prepared by the hydrogenation of *trans*-octahydronaphthalene, b. p. 189°/768 mm., $d_4^{20\ vac.}$ 0·9009, n_α^{20} 1·48504, which is derived from *trans*-decahydro-β-naphthol, m. p. 75° (cf. Häckel, *loc. cit.*), by the action of potassium hydrogen sulphate. The optical constants of the authors' *cis*-decahydronaphthalene agree closely with those of the specimens prepared by Häckel (*loc. cit.*) and Willstätter and Seitz (this vol., i, 628). This is not the case with the *trans*-derivatives. It appears, therefore, that the product of the hydrogenation of naphthalene in the presence of nickel contains some component other than *trans*-decahydronaphthalene which tends to accumulate in the fractions of lowest boiling point. H. W.

Internal Structure of Crystallised Carbon and Benzene. J. Beckenkamp.—(See ii, 754.)

Mechanism of Substitution Reactions in the Aromatic Nucleus. E. de B. Barnett and J. W. Cook (*Rec. trav. chim.*, 1924, **43**, 262—265).—The possibility is considered of the formation of *cis* and *trans* geometrically isomeric unstable additive compounds in substitution reactions in the aromatic nucleus. The facts that *p*-chlorobromobenzene is almost the sole product in the bromination of chlorobenzene, no *p*-dibromobenzene being formed, and that bromonitrobenzene is alone produced in the nitration of bromobenzene, are explained by assuming that the intermediate additive compound has the *trans* configuration in each case. The type of isomerism here assumed is analogous to the isomerism of the esters of $\Delta^{2:5}$-dihydroterephthalic acids established by Baeyer. In the anthracene series, but not in the benzene series, several such additive compounds, for instance, the esters of nitrodihydroanthranol, have been isolated. J. K.

Replaceability of the Halogen Atom in Chloro- and Bromo-4-nitro-2-cyanobenzene. H. P. Baudet (*Rec. trav. chim.*, 1924, **43**, 707—726).—The reactivity of the halogen atom in these compounds is studied and compared with that of the halogen in chloro- and bromo-2 : 4-dinitrobenzenes and in chloro- and bromo-2-nitro-4-cyanobenzenes. In this way, the influence of the cyano group on the reactivity of the adjacent halogen atom is estimated. The reactivity of the chlorine in chloro-4-nitro-2-cyanobenzene is demonstrated by its direct replacement to give the following compounds: 4-nitro-2-cyanoanisole; 4-nitro-2-cyanophenetole; 4-*nitro*-2-*cyanodiphenyl ether*, m. p. 129° (by the action of phenol and sodium ethoxide); p-*nitro*-2-*cyanoaniline*, m. p. 209°; 4-*nitro*-2-*cyanomethylaniline*, m. p. 187°, which gives with concentrated nitric acid 4 : 6-*dinitro*-2-*cyanophenylmethylnitroamine*, m. p. 100°; 4-*nitro*-2-*cyanoethylaniline*, m. p. 144°, which gives 4 : 6-*dinitro*-2-*cyanophenylethylnitroamine*, m. p. 89°; 4-*nitro*-2-*cyanodimethyl*-

aniline, m. p. 110°; 4-nitro-2-cyanodiphenylamine, m. p. 172° (by the action of aniline); *4-nitro-2-cyanophenyl*-m-*tolylamine*, m. p. 142°; *4-nitro-2-cyanophenyl*-p-*tolylamine*, m. p. 218°; *4-nitro-4'-amino-2-cyanodiphenylamine*, m. p. 204° (by the action of phenylhydrazine); 4-nitro-2-cyanophenylhydrazine (by the action of hydrazine hydrate), giving *benzaldehyde-4-nitro-2-cyanophenylhydrazone*, m. p. 206°; *4-nitro-2-cyanohydrazobenzene*, m. p. 236°. Aniline, phenylhydrazine, and the toluidines react more readily with chloro-4-nitro-2-cyanobenzene than with chloro-2-nitro-4-cyanobenzene. With chloro-4-nitro-2-cyanobenzene, *p*-toluidine reacts more readily than *o*-toluidine, but less readily than *m*-toluidine. Methylaniline has no action on chloro-4-nitro-2-cyanobenzene. 4-Nitro-2-cyanophenylhydrazine has no action on acetone, whereas *p*-nitrophenylhydrazine readily reacts. Measurements of the velocity constants of the reaction between sodium methoxide or ethoxide and chloro- or bromo-4-nitro-2-cyanobenzene in absolute alcohol are given. Chlorine is more readily replaced than bromine and the velocity constant for sodium methoxide is smaller than that for sodium ethoxide. When the 2-nitro group of chloro-2 : 4-dinitrobenzene is replaced by a cyano group, the velocities of the actions of both sodium methoxide and ethoxide are decreased. Interchange of the cyano and nitro groups of the halogeno-4-nitro-2-cyanobenzenes reduces the velocity constants to about one-nineteenth. The velocity of the reaction of *p*-chloronitrobenzene with sodium methoxide is about 1/7500 of the velocity of the reaction of chloro-4-nitro-2-cyanobenzene with the same substance. In 90% alcohol, the velocity of the action of sodium methoxide on the halogeno-4-nitro-2-cyanobenzenes is greater than in absolute alcohol; the increase is greater for the chloro compound than for the bromo compound. On the other hand, with sodium ethoxide in 90% alcohol, k is smaller and the decrease is greater for the chloro compound than for the bromo compound. Measurements of k are given for the action of sodium methoxide on chloro-2 : 4-dinitrobenzene in mixtures of methyl alcohol and water. As the proportion of water in the medium is increased, a maximum in the value of k is reached; this occurs the sooner the higher the temperature. W. E. E.

Monochlorotrinitrobenzenes and the Replacement of their Substituents. P. G. Van de Vliet (*Rec. trav. chim.*, 1924, 43, 606—635).—*Chloro*-3 : 4 : 5-*trinitrobenzene*, m. p. 168°, is obtained by the action of a mixture of nitric oxide and nitrogen peroxide at 0° on 4-chloro-2 : 6-dinitroaniline (from 1 : 4-dichloro-3 : 5-dinitrobenzene and alcoholic ammonia) mixed with concentrated nitric acid.

Chloro-2 : 3 : 5-trinitrobenzene is obtained from aceto-*m*-nitroanilide by nitrating with fuming nitric acid (d 1·52) in the presence of sulphuric acid and hydrolysing the 2 : 3-dinitroacetanilide separated from the resulting mixture of three isomerides; the dinitroaniline is diazotised, converted by cuprous chloride into chloro-2 : 3-dinitrobenzene, and nitrated in the presence of fuming

sulphuric acid. The semi-solid product is separated into an oil and *chloro*-2 : 3 : 5-*trinitrobenzene*, m. p. 105—106°. Its structure is confirmed by conversion into chloro-3 : 5-dinitroaniline.

Chloro-2 : 3 : 4-*trinitrobenzene*, m. p. 68°, is prepared from the oil resulting from the above nitration, and its structure is confirmed by its conversion into a chlorodinitroaniline which yields chloro-2 : 4-dinitrobenzene.

Chloro-2 : 3 : 6-trinitrobenzene is not formed in the nitration of chloro-2 : 3-dinitrobenzene, and seven other methods of preparing this isomeride were tried unsuccessfully.

Den Hollander (A., 1920, i, 538) claims to have prepared 1 : 2-dichloro-3 : 6-dinitrobenzene (m. p. 60°). His experiments were repeated, starting from a mixture of 2 : 3- and 2 : 5-dinitroacetanilide. After hydrolysis, the 2 : 5-dinitroaniline (m. p. 138°) was dissolved in concentrated hydrochloric acid and treated with potassium chlorate. The mixture of chlorodinitroanilines thus obtained was diazotised and the diazo compounds were treated with cuprous chloride solution. 1 : 4-Dichloro-2 : 5-dinitrobenzene was isolated, and 1 : 4 : 6-trichloro-2 : 5-dinitrobenzene (m. p. 60°) was obtained from the mother liquor (A., 1921, i, 549).

To study the behaviour of the chlorotrinitrobenzenes towards sodium methoxide, the reaction mixture is poured into water and this is tested for chlorine and nitrite ions. In this way, it is shown that, in the following compounds, only the groups mentioned are replaced by methoxyl: chloro-2 : 4 : 6-trinitrobenzene, chloro; chloro-3 : 4 : 5-trinitrobenzene, 4-nitro; chloro-3 : 4 : 6-trinitrobenzene, chloro and 3-nitro; chloro-2 : 3 : 5-trinitrobenzene, 2-nitro; chloro-2 : 3 : 4-trinitrobenzene, chloro and 3-nitro. In the action of sodium methoxide on 1 : 3-dichloro-2 : 4-dinitrobenzene, it is the 3- and not the 1-chlorine atom which is replaced.

Owing to the considerable velocities developed in the reactions between sodium methoxide and the chlorotrinitrobenzenes all quantitative experiments were carried out at 0°. In the cases of the 1 : 2 : 4 : 6-, 1 : 3 : 4 : 6-, and 1 : 2 : 3 : 5-isomerides, the velocities were too great to be determined. For the 1 : 3 : 4 : 5-isomeride, $k=7{\cdot}5$ (approx.), and for the 1 : 2 : 3 : 4-isomeride, $k=10{\cdot}7$ (approx.), the constant being calculated from the formula $dx/dt=k(a-x)^2$.

Den Hollander's rules (*loc. cit.*) for the action of sodium methoxide on chloronitro derivatives of benzene prove to be of very limited application, and the following empirical conclusion is drawn. When sodium methoxide reacts with chloronitrobenzene derivatives, the substituents which are *meta* with respect to a nitro group tend to be inactive, whilst those that are *ortho* or *para* with respect to a nitro group tend to be replaced. It is concluded that the introduction of a nitro group into a chloronitro derivative of benzene causes a much greater increase in the reactivity of the substituents than does the introduction of a chlorine atom. W. E. E.

Mononitration of *p*-Chlorotoluene. H. H. Hodgson and P. Anderson (*J. Chem. Soc.*, 1924, **125**, 2195—2196).—4-Chloro-2-nitrotoluene and 4-chloro-3-nitrotoluene, obtained on nitrating

p-chlorotoluene under various conditions (or by the Sandmeyer reaction from the corresponding nitrotoluidines), are quantitatively converted into 4-chloro-*o*-toluidine (I) and 3-amino-*p*-tolyl mercaptan (II), respectively, by boiling with sodium di- or tri-sulphide in alcoholic solution. The quantities of I and II in the reduction product are found: (*a*) by titration of each after separation by steam distillation; (*b*) by diazotisation, when II is converted into the insoluble diazosulphide, $C_7H_6<^{N}_{S}{}^{2}$, whilst diazotised I is coupled with β-naphthol and the azo compound weighed. The figures obtained by this method of analysis agree very closely with those calculated by interpolation and extrapolation of Holleman's cryoscopic data (A., 1909, i, 18). A. C.

Ammonium as a Reducing Agent. H. H. Schlubach and H. Miedel (*Ber.*, 1924, **57**, [*B*], 1682—1686).—A solution of sodium in liquid ammonia is added gradually to a solution of ammonium chloride in the same solvent in which the substance to be reduced is at least partly dissolved at −80° to −50°. If the compound under investigation is not sufficiently soluble in liquid ammonia, benzene or ether may be added. In general, reduction appears to be due to the direct addition of nascent hydrogen without preliminary formation of an intermediate additive compound with the sodium. The action is highly selective and appears to resemble most closely that of sodium and alcohol. Probably owing to the low temperature of the reactions, the formation of by-products is largely avoided.

Phenylbutylene is smoothly hydrogenated to phenylbutane, whereas cinnamic acid and stilbene remain unchanged. Benzophenone is converted directly into diphenylmethane; the intermediate production of benzhydrol could not be established. On the other hand, Michler's ketone, didiphenylyl ketone, benzil, benzoin, and deoxybenzoin are unaffected. Acetophenone could not be reduced, whereas β-phenylethyl methyl ketone readily yields α-phenylbutan-γ-ol. The latter substance is also obtained with rather greater difficulty from styryl methyl ketone. Less favourable results were obtained with 1 : 3-dimethyl-Δ^6-*cyclo*hexen-5-one and methylheptenone. Benzene is unaffected, whereas pyridine is converted into piperidine. Nitrobenzene is transformed into aniline. H. W.

Synthesis of Diaryl Compounds by means of the Diazo Reaction. M. Gomberg and W. E. Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2339—2343).—In the formation of diaryl compounds by Bamberger's method (A., 1896, i, 299) the isolation of the unstable explosive diazonium oxides (or diazo anhydrides) is unnecessary. Both symmetrical and unsymmetrical diaryl compounds may be obtained by diazotising the amine in the usual manner, adding the hydrocarbon, and slowly adding to the cooled, well-stirred mixture a 15 to 25% sodium hydroxide solution until the mixture contains about 1 to 2% of free alkali. Equally good

results were obtained by adding benzenediazonium chloride to a well-stirred mixture of benzene and sodium hydroxide solution, the solution at the end containing 2% of free alkali. It is suggested that the normal sodium diazotate is first produced and that this undergoes partial hydrolysis: $2RN_2\cdot ONa+2H_2O \rightleftharpoons 2RN_2\cdot OH+2NaOH$; $2RN_2\cdot OH \rightleftharpoons RN_2\cdot O\cdot N_2R+H_2O$. With benzene and benzenediazonium chloride, in addition to diphenyl, *p*-phenyldiphenyl and more complex products are produced by the diazo compound coupling with the diaryl compound first formed (cf. Gerngross and Dunkel, this vol., i, 720).

The following compounds have been prepared by this method (the figures in brackets denote yields in % of theory): From aniline, diphenyl (22%), phenylthiophen (11%), *p*-cyanodiphenyl (10%), *o*- and *p*-bromodiphenyl, methyl diphenyl-4-carboxylate, *p*-nitrodiphenyl, and phenylpyridine. From *p*-bromoaniline, *p*-bromodiphenyl (40—46%), p-*bromophenylthiophen*, m. p. 100° (20%); from *m*-bromoaniline, m-*bromodiphenyl*, b. p. 299—301° (28%); from *p*-chloroaniline, *p*-chlorodiphenyl (41%), p-*chlorophenylthiophen*, m. p. 83° (24%); from *m*-chloroaniline, m-*chlorodiphenyl*, b. p. 284—285° (27%); from *p*-nitroaniline, *p*-nitrodiphenyl (30%), p-*nitrophenylthiophen*, m. p. 137—138° (23%); from *m*-nitroaniline, *m*-nitrodiphenyl (18%); from *o*-nitroaniline, *o*-nitrodiphenyl; from *p*-cyanoaniline, *p*-cyanodiphenyl (15%); from *m*-cyanoaniline, m-*cyanodiphenyl*, m. p. 49° (19%), m-*cyanophenylthiophen*, m. p. 53—54° (15%); from *p*-aminodiphenyl, *p*-phenyldiphenyl; and from ethyl *p*-aminobenzoate, ethyl diphenyl-4-carboxylate (12%).

R. B.

Action of Nitric Acid on αα-Diphenylethylene and αα-Di-*p*-tolylethylene. II. R. Anschütz and A. Hilbert (*Ber.*, 1924, **57**, [*B*], 1697—1700; cf. Anschütz and Hilbert, A., 1921, i, 783; Konovalov and Jatzewitsch, A., 1905, i, 763).—β-Nitro-αα-diphenylethyl alcohol is converted by reduction with granulated zinc and glacial acetic acid into β-amino-αα-diphenylethyl alcohol, m. p. 110°, whereas stannous chloride transforms it into benzophenone and methylamine. β-Nitro-α-ethoxy-αα-diphenylethane, m. p. 91—92° (cf. Konovalov and Jatzewitsch, *loc. cit.*), and β-*nitro-α-methoxy-αα-diphenylethane*, m. p. 139°, are described. Di-*p*-tolylethylene, b. p. 163—165°/13 mm., m. p. 61°, is prepared by the action of magnesium *p*-tolyl bromide on ethyl acetate and subsequent distillation of the product. It is converted by bromine in carbon disulphide solution into β-*bromo-αα-di*-p-*tolylethylene*, m. p. 67°, and is reduced by sodium and alcohol to αα-di-*p*-tolylethane, b. p. 155—157°/12 mm. The hydrocarbons are converted by nitric acid in glacial acetic acid solution into β-*nitro-αα-di*-p-*tolylethylene*, m. p. 116°, which is oxidised by chromic acid to di-*p*-tolyl ketone. p-*Nitro-α-ethoxy-αα-di*-p-*tolylethane*, prepared by the action of sodium ethoxide on β-nitro-αα-di-*p*-tolylethylene, has m. p. 95°.

H. W.

Partition of Silver Nitrate between Aniline and Water. A. Frumkin and R. Kulvarskaja.—(See ii, 757.)

Action of Aromatic Amines on Semicarbazide Hydrochloride. H. MAZOUREWITCH (*Bull. Soc. chim.*, 1924, [iv], **35**, 1183—1186).—The *s*-diphenylcarbamide formed as a by-product in the action of aniline on the semicarbazidesemicarbazones of mesityl oxide and 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone (this vol., i, 969) probably results from the decomposition of the semicarbazidesemicarbazones, since it is now shown that the action of boiling aromatic amines on semicarbazide hydrochloride yields the corresponding substituted carbamide, the suggested mechanism of the reaction being as follows: $R{\cdot}NH_2+NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2=NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_3$; $NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_2R=(NHR)_2CO+(NH_2)_2$. Thus aniline and semicarbazide hydrochloride yield *s*-diphenylcarbamide, m. p. 233—235° (decomp.); similarly, *o*-toluidine yields *s*-di-*o*-tolylcarbamide, m. p. 237—239° (decomp.); *p*-toluidine, *s*-di-*p*-tolylcarbamide, m. p. 248—253° (decomp.); 3-*o*-xylidine, *s*-di-*o*-xylylcarbamide, m. p. 242° (decomp.), and benzylamine, *s*-dibenzylcarbamide, m. p. 168°. With *p*-aminoacetophenone and *p*-bromoaniline, the reaction is more complicated and definite products have not been isolated. R. B.

Velocity of Benzylation of certain Amines. D. H. PEACOCK (*J. Chem. Soc.*, 1924, **125**, 1975—1980).—Aniline and other amines have been benzylated by means of benzyl chloride and *p*-nitrobenzyl chloride and the reaction velocity constants determined from the expression used by Menschutkin (cf. A., 1890, 1366; 1900, 335) and also from an amended expression which takes into account the action of amine on the hydrochloride formed. Both equations give similar results for the initial stages, but that of Menschutkin agrees better with the later stages in spite of the above consideration. The following values were found for k_{35}, k_{45}, and E (the energy of activation): Aniline–benzyl chloride, 0·00157, 0·00315, 13454 cal.; aniline–*p*-nitrobenzyl chloride, 0·000588, 0·00125, 14678 cal.; *p*-toluidine–benzyl chloride, 0·00217, 0·00495, 16050 cal.; *p*-toluidine–*p*-nitrobenzyl chloride, 0·00137, 0·00252, 11860 cal. The value E is calculated from $\log k_1/k_2=E/R(1/T_2-1/T_1)$. The value of the velocity coefficients changes with the concentration of the reactants and particularly of the amine. Values of k are given for the reaction of 9 bases with benzyl chloride in alcohol at 40°. The following benzylated amines and their benzoyl (A) and *p*-toluenesulphonyl (B) derivatives were isolated: *Benzyl*-o-*chloroaniline*, m. p. 44°, (A) m. p. 111°; *benzyl*-p-*chloroaniline*, m. p. 45°, (A) m. p. 138°; *benzyl*-2 : 5-*dichloroaniline*, m. p. 47°, (A) m. p. 69°; *benzylaniline*, (A) m. p. 105°, (B) m. p. 133°; *benzyl*-o-*toluidine*, (A) m. p. 65°; *benzyl*-p-*toluidine*, (A) m. p. 127°, (B) m. p. 126°. A. C.

Chlorine or Bromine Derivatives obtained by the Aid of Mixtures of Hydrogen Peroxide and the Corresponding Halogen Acids. A. LEULIER (*Bull. Soc. chim.*, 1924, [iv], **35**, 1325—1330).—A mixture of hydrogen peroxide and hydrochloric or hydrobromic acid is a satisfactory source of nascent halogen for the preparation of aromatic bromo or chloro derivatives.

The following compounds were prepared in this way: *p*-Chloroacetanilide (poor yield), 3 : 5-dichloro-*o*-nitroaniline, 2 : 6-dichloro-*p*-nitroaniline (74% yield), a *chloro*-2 : 4-*dinitroaniline* (m. p. 131—132°), 5-chloroaceto-*o*-toluidide (poor yield), 3-chloro-5-nitro-*o*-toluidine, chloroaceto-*p*-phenetidide (m. p. 123—124°), 5-bromoaceto-*o*-toluidide, 3-bromo-5-nitro-*o*-toluidine. Brominations proceed more satisfactorily than chlorinations. W. E. E.

Magnesium Anilide. A. TERENTIEFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 1164—1168).—In the absence of air, magnesium reacts with aniline vapour at 370—380° under atmospheric pressure, yielding magnesium anilide, $(NHPh)_2Mg$, a light yellow powder. The product is unstable in air and rapidly blackens; its composition was accordingly calculated from the amounts of aniline consumed and of hydrogen liberated out of contact with air. Magnesium anilide is violently decomposed by water with regeneration of aniline (cf. Meunier, A., 1903, i, 544); alcohol vapour at 100—110° causes a similar decomposition, yielding aniline. With ethyl acetate vapour at 200°, acetanilide is produced (cf. Bodroux, A., 1904, i, 662; 1905, i, 585). In a current of dry air at 100°, profound oxidation takes place, but a small quantity of azobenzene was the only product isolated; the reaction with oxygen is explosive. Carbon dioxide at 180° yields magnesium phenylcarbamate, $(NHPh{\cdot}CO_2)_2Mg$ (cf. Houben, A., 1904, i, 1104; 1909, i, 921), which on heating at 250—270° is decomposed into magnesium oxide, carbon dioxide, and *s*-diphenylcarbamide. R. B.

New Types of Ter- and Quadri-valent Compounds of Manganese. F. OLSSON (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 10, 5—9).—When solutions of chlorides of organic bases in absolute alcohol, saturated with hydrogen chloride, are mixed with manganese trichloride solution obtained by reduction of potassium permanganate in alcoholic solution by means of hydrogen chloride (cf. Meyer and Best, A., 1900, ii, 77), double salts with chlorides of quaternary ammonium bases, $2RCl,MnCl_3$ (R=an organic base), are obtained. The formation of these compounds is probably determined by their low solubility in alcohol. Such pentachloromanganates are green and are free from solvent in the form of alcohol of crystallisation. The compounds prepared were: $(NMe_4)_2MnCl_5$; $(NEt_4)_2MnCl_5$; $(NPr_4)_2MnCl_5$; $(NPhMe_3)_2MnCl_5$; $(NPhEt_3)_2MnCl_5$; $(NPhMe_2Et)_2MnCl_5$; $(NPhMeEt_2)_2MnCl_5$; $(NHMe_3Et)_2MnCl_5$; $(NMe{\cdot}C_{10}H_8Me)_2MnCl_5$; $(NEt{\cdot}C_{10}H_8Me)_2MnCl_5$; $(NMe_3{\cdot}C_6H_4Me)_2MnCl_5$; $(NPhMeEtPr)_2MnCl_5$. When the compound $NEt_4{\cdot}MnO_4$, obtained from silver permanganate and tetraethylammonium chloride, is reduced by acetic acid and dry hydrogen chloride is passed through the solution, the reddish-brown *compound*, $NEt_4{\cdot}MnCl_4,2C_2H_4O_2$, gradually separates.

The double iodates, $K(Rb,Cs,NH_4)_2Mn(IO_3)_5$, prepared by the action of the alkali iodates on the compound $Mn(OAc)_3,2H_2O,HIO_3$, crystallise in yellow or yellowish-brown, doubly-refracting, cube-like octahedra, and are more stable in the air and towards the usual reagents than the double chlorides.

The following periodates of tervalent manganese, $(M''O,Mn_2O_3,I_2O_7,xH_2O)$, prepared by Price's method (A., 1903, ii, 652), form red crystals, but turn brown at 110°, with loss of their water of crystallisation: $M=H_2$, $x=5$; $M=Na_2$, $x=3$; $M=K_2$, $x=2$; $M=Sr$, $x=3$; $M=Mg$, $x=3$; $M=(CH_6N_3)_2$, $x=8$; $M=Ag_2$, $x=0$; $M=Cd$, $x=4$; $M=Zn$, $x=4$; $M=Cu$, $x=3$; $M=Pb$, $x=3$.

The *compound* $Mn(CHBzAc)_3$, prepared from benzoylacetone and manganese acetate, forms microscopic, stellar aggregates of green prisms, m. p. 168·5°.

By the action of manganese tetrachloride, prepared by Weinland and Dinkelacker's method (A., 1909, ii, 48), on different chlorides at the temperature of solid carbon dioxide, the following double chlorides are obtained as black crystals: $(NMe_4)_2MnCl_6$; $(NPhMe_3)_2MnCl_6$; $(NMe_3{\cdot}C_6H_4Me)_2MnCl_6$; $(NPhMe_2Et)_2MnCl_6$; $(NPhMeEt_2)_2MnCl_6$. Double iodates of quadrivalent manganese having the formulæ $Rb_2Mn(IO_3)_6$ and $Cs_2Mn(IO_3)_6$ are obtainable by the action of iodic acid and alkali iodate on manganese dioxide suspended in water (cf. Berg, A., 1899, ii, 426). The corresponding barium salt, described by Berg, is obtainable more readily by dissolving manganese triacetate, barium iodate, and iodic acid in 10% nitric acid.

Periodates of quadrivalent manganese $(M''O,2MnO_2,I_2O_7,xH_2O)$ may be obtained as crystalline powders by the interaction of manganic acetate, 10% nitric acid, and periodates. The following were prepared: $M=H_2$, $x=5$; $M=Na_2$, $x=2$; $M=K_2$, $x=1{\cdot}5$; $M=Ca$, $x=4$; $M=Sr$, $x=4$; $M=Mg$, $x=3$; $M=Ag_2$, $x=2$; $M=(CH_6N_3)_2$, $x=10$; $M=Cd$, $x=5$; $M=Zn$, $x=3{\cdot}5$; $M=Cu$, $x=4$; $M=Pb$, $x=2$; also $Al_2O_3,4MnO_2,2I_2O_7,10H_2O$. T. H. P.

Quinquevalent Chromium. F. Olsson (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 10, 10—12).—The addition to a solution of chromium oxychloride of chlorides of organic bases dissolved in concentrated acetic acid saturated with hydrogen chloride (cf. Weinland and Fiederer, A., 1907, i, 549; ii, 31) yields double chlorides of the form $RCl,CrOCl_3$; variation of the proportions of the reagents within wide limits is without influence on the composition of the resulting compounds, which form reddish- or yellowish-brown, rhombic tablets and are moderately stable in dry air. Such are: NMe_4CrOCl_4; NEt_4CrOCl_4; NPr_4CrOCl_4; $NPhMe_3CrOCl_4$; $NPhEt_3CrOCl_4$; $NPhMe_2EtCrOCl_4$; $NPhMeEt_2CrOCl_4$; $NMe(C_{10}H_8Me){\cdot}CrOCl_4$; $NEt(C_{10}H_8Me){\cdot}CrOCl_4$; $NMe_3(C_6H_4Me){\cdot}CrOCl_4$; $NPhMeEtPrCrOCl_4$.

Addition of an aqueous solution of the compound $4CrO_3,Cr_2O_3$ to excess of a solution of potassium fluoride in 40% hydrofluoric acid at 0° yields the compound KF,CrO_2F,H_2O as a yellowish-brown precipitate. T. H. P.

Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen. J. Meisenheimer, L. Angermann, O. Finn, and E. Vieweg (*Ber.*, 1924, **57**, [*B*], 1744—1759).—Although the

existence of an asymmetric, saturated, tervalent nitrogen atom has frequently been assumed in order to account for the formation of stereoisomeric compounds containing this atom, no substance of this class has hitherto been resolved into optically active components. With this end in view, a large number of tertiary amines, particularly such as contain the acetonyl and phenacyl groups, which appear to exert a favourable influence on the resolution of sulphonium compounds, have been examined with entirely negative results. It is therefore concluded that saturated, tervalent nitrogen, unless present in a particular manner in a polycyclic ring system, seldom if ever causes the phenomenon of stereoisomerism; this conclusion is in harmony with the observations of Pope and his co-workers (T., 1904, **85**, 1330; 1907, **91**, 458; 1910, **97**, 2199). The attribution of the non-resolvability of these compounds to the presence of the three radicals attached to the nitrogen atom in the same plane as the nitrogen atom involves difficulties in other directions, so that it is assumed that this is only a mean position around which the atoms in ammonia and the amines constantly oscillate. Stabilisation occurs only when the fourth co-ordination position of the nitrogen atom is occupied by a positively charged hydrogen atom or an alkyl residue (ammonium compounds), an oxygen atom (amine oxides), or a complex metallic residue (ammines). According to Werner's theory, a close analogy exists between the amines and the ions of sulphonium salts, [Sabc]X. Since, however, the former are non-resolvable whereas the latter have been resolved, this analogy cannot be fully maintained. It appears more probable that the central sulphur atom is co-ordinatively quadrivalent and that when sulphonium salts become ionised the tetrahedral disposition of the radicals is maintained by the immediate substitution of water for halogen : $\begin{bmatrix} Me \\ Me \end{bmatrix}\!S\!\begin{matrix} Me \\ Cl \end{matrix}\Big] \xrightarrow[\text{in water}]{\text{solution}} \begin{bmatrix} Me \\ Me \end{bmatrix}\!S\!\begin{matrix} Me \\ Aq \end{matrix}\Big]Cl$.

1-*Methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* d-*π-bromocamphorsulphonate*, $C_{10}H_{12}N\cdot C_{10}H_{15}O_4BrS$, prepared from its components in ethyl acetate, has m. p. 141° (decomp.), $[M]_D$ +276° in ethyl alcohol; the corresponding *monohydrate* has m. p. 137°. Diethylaniline gives a d-*π-bromocamphorsulphonate*, m. p. 222—223°, $[M]_D$ +272° in alcohol. Ethylaniline gave with a somewhat old specimen of the acid mainly *ethylaniline* d-*π-bromocamphorsulphonate*, m. p. 146·5—148° (*monohydrate*, m. p. about 80°), together with smaller amounts of a *salt*, $C_8H_{11}N,C_{16}H_{10}O_4BrS$, m. p. 195—196°, which is probably derived from *d-iso*bromocamphorsulphonic acid (cf. Kipping, T., 1905, **87**, 635). *Ethylpropylaniline* d-*π-bromocamphorsulphonate* has m. p. 137—138°.

Acetonylmethylethylamine, $C_6H_{13}ON$, an unstable liquid, b. p. 44—45°/15 mm., prepared from methylethylamine and chloroacetone in ethereal solution, yields a *picrate*, m. p. indefinite, 80—85°, and a d-*α-bromocamphor-π-sulphonate*, m. p. 115—122°, $[M]_D$ +275°. *Phenacylmethylethylamine*, b. p. 130—131°/11 mm., the *picrate*, m. p. 116—118° after previous softening, and the d-*bromocamphorsulphonate*, m. p. 141—142° after softening at 137°, $[M]_D$

+276°, are described. Methylaniline and chloroacetone give a mixture of 1 : 3-*dimethylindole*, b. p. 119—120°/7 mm. (*picrate*, m. p. 141—143°), much unchanged methylaniline, and *acetonylmethylaniline*, b. p. 135—136°/8 mm.; the latter substance yields a crystalline *picrate*, but its salts with optically active acids could not be caused to crystallise. 1-*Acetonyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 178°/17 mm., m. p. 39—41°, gives a d-*bromocamphorsulphonate*, m. p. (indefinite) 110—116°, $[M]_D$ +265°. 1-*Phenacyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 101—103°, and its d-*bromocamphorsulphonate*, m. p. (indefinite) 110—135°, are described; the base recovered from the salt was optically inactive. *Acetonylmethylcyclohexylamine*, b. p. 106°/11 mm., does not yield a crystalline bromocamphorsulphonate; the *picrate* has m. p. 162—163° after previous softening. The amine absorbs oxygen when dissolved in ether and becomes converted into *benzoylmethylcyclohexylamine*, m. p. 130—135°.

N-*Phenyl*-N-p-*tolylanthranilic acid*, m. p. 173°, prepared from phenylanthranilic acid, *p*-iodotoluene, copper powder, and potassium carbonate in the presence of nitrobenzene at 200—215°, is readily purified through the sparingly soluble, tetrahydrated *sodium* salt; it could not be resolved by means of the *strychnine* salt, m. p. 184—185°, or *quinine* salt ($+C_6H_6$), m. p. 154—164°; the cinchonine, brucine, and morphine salts do not crystallise satisfactorily. *Phenyl*-α-*naphthylanthranilic acid*, m. p. 226°, could not be resolved by means of its *brucine* salt ($+1{\cdot}5H_2O$), m. p. 237°, or *morphine* salt ($+4H_2O$), m. p. 174° (decomp.) after softening at 155°. H. W.

Derivatives of Diphenylamine. E. Papasogli (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 106—110).—p-*Bromo*-p′-*nitrodiphenylamine*, $C_6H_4Br{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, prepared by treating *p*-nitrodiphenylamine with a mixture of sulphuric acid, bromine, and pyridine (or quinoline) in acetic acid solution, forms orange-yellow crystals, m. p. 162°. When subjected in acetic acid solution to a current of nitrous anhydride, it is converted into the required *nitrosoamine*, $C_6H_4Br{\cdot}N(NO){\cdot}C_6H_4{\cdot}NO_2$, m. p. 151°, which yields *p*-bromo-*p*′-nitrodiphenylamine when treated with hydroxylamine hydrochloride in alcoholic solution. T. H. P.

Derivatives of *ac*-Tetrahydro-β-naphthylamine. A. Windaus [with O. Dalmer, H. Schreiterer, R. Hupe, and H. Köcher] (*Ber.*, 1924, **57**, [*B*], 1731—1739).—2-Amino-7-hydroxynaphthalene is reduced by sodium and amyl alcohol to a mixture of 2-*amino*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 168·5°, and 2-*amino*-7-*hydroxy*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, which can be separated from one another, since only the former is soluble in sodium hydroxide solution; it yields a *hydrochloride*, m. p. 166·5°, a *picrate*, m. p. 205° after softening, and a *dibenzoyl* derivative, m. p. 174° after softening; 2-*acetamido*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* has m. p. 195°. The base is converted by bromine in glacial acetic acid solution into 6 : 8-*dibromo*-2-*amino*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 251° (decomp.),

after darkening at 215° (*hydrobromide*, m. p. 284°; *diacetyl* derivative, m. p. 187°). The action of nitric acid on a solution of 2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene in glacial acetic acid leads to the almost immediate separation of the *nitrate* of nitro-2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene; the corresponding free *base*, m. p. 236° (decomp.), its *hydrochloride*, decomp. 260—310°, and *diacetyl* derivative, m. p. 178°, are described. The filtrates from the nitrate described above gradually deposit the nitrate of 6 : 8-dinitro-2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene; the free *base*, m. p. 243° (decomp.), the *hydrochloride*, decomp. 220—290°, and the *diacetyl* derivative, m. p. 193° (decomp.), are described. The portion of the product of the reduction of 2-amino-7-hydroxynaphthalene which does not dissolve in sodium hydroxide (see above) is separated by light petroleum into 2-amino-7-hydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene, m. p. 141·5°, b. p. 200—210°/12·5 mm. (*hydrochloride*, m. p. 236°; *picrate*, m. p. 181°), and ar-2-*aminodihydronaphthalene*, b. p. 150—155°/14 mm., m. p. 53° (*picrate*, m. p. 194° [decomp.]; *dibromo* compound, $C_{10}H_{11}NBr_2$, m. p. 62°); the *picrate* of *ar*-2-aminotetrahydronaphthalene has m. p. 204° (decomp.).

2-*Amino*-7-*methoxynaphthalene*, m. p. 143° (*hydrochloride*, m. p. 222—223° [decomp.]; *picrate*, decomp. 165°; *acetyl* derivative, m. p. 156°), is prepared by the action of ammonium sulphite and ammonia on 2-hydroxy-7-methoxynaphthalene at 150—160°. It is reduced by sodium and boiling amyl alcohol to a mixture of the corresponding tetrahydro derivatives, which is separated into its components by treatment of its ethereal solution with carbon dioxide, whereby 2-amino-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene is precipitated as the *carbonate* (? *carbamate*); the free *base*, a colourless liquid, *hydrochloride*, m. p. 213°, *picrate*, decomp. about 212° after softening, and *picrolonate*, decomp. about 252°, are described. The base is converted by hydriodic acid into 2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. The physical constants of the *hydrochloride*, m. p. 225°, *picrate*, m. p. 183° (decomp.), and *acetyl* derivative, m. p. 93°, of 2-amino-7-methoxy-5 : 6 : 7 : 8-tetrahydronaphthalene, are given with reserve as the complete freedom of the base from the isomeric 1 : 2 : 3 : 4-tetrahydro compound is not established. 2-*Hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, prepared by the catalytic hydrogenation of 2-hydroxy-7-methoxynaphthalene in the presence of spongy palladium, has m. p. 71°.

2 : 7-Diaminonaphthalene (*dipicrate*, m. p. 210°; *diacetyl* derivative, m. p. 261°; *dibenzoyl* derivative, m. p. 267°) is reduced by sodium and boiling amyl alcohol to 2 : 7-*diamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 162°/20 mm., m. p. about 60° (*hydrochloride*, m. p. about 360° [decomp.]; *diacetyl* derivative, m. p. 203°; *dibenzoyl* compound, m. p. 255°). It is transformed by nitrous acid into 2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene.

The following derivatives of 2 : 6-dihydroxynaphthalene are described: the *monomethyl ether*, m. p. 136—137°; 2-*amino*-

6-*methoxynaphthalene*, m. p. 139—140° (*hydrochloride*, m. p. 181°; *acetyl* derivative, m. p. 159—160°). 2 : 6-*Diaminonaphthalene*, m. p. 216—217°, is smoothly reduced to 2 : 6-*diamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 61°; the *hydrochloride*, diacetyl derivative, m. p. 240°, and *dibenzoyl* compound, m. p. 258°, are described. H. W.

Nitrophenyl Ethers and their Halogen Substitution Products. O. MATTER (D.R.-P. 386618; from *Chem. Zentr.*, 1924, i, 2632).—Nitrophenyl ethers are prepared by heating mono- or poly-halogenated nitrohydrocarbons with monohydric alcohols and feebly basic metal hydroxides, carbonates, or hydrogen carbonates, with or without the addition of catalysts. For example, *p*-chloronitrobenzene yields *p*-nitroanisole on heating at 175—185° with sodium carbonate and diluted methyl alcohol; at 200—210° with sodium carbonate, ethyl alcohol, and copper powder, *p*-nitrophenetole is formed. With slight variations in the conditions 3 : 4-dichloronitrobenzene yields 2-chloro-4-nitroanisole, m. p. 95°, and 2 : 5-dichloronitrobenzene yields 4-chloro-2-nitroanisole, m. p. 95°, and 4-chloro-2-nitrophenetole, m. p. 61—62°. F. A. M.

Solubility and Partition Measurements of Picric Acid in Solutions of Salts. E. SCHREINER (*Z. anorg. Chem.*, 1924, **138**, 311—321).—By means of measurements of conductivity and catalytic power, the value K_0=0·31 at 25° is found for the dissociation constant of picric acid in water on the basis of Bjerrum's theory (A., 1919, ii, 9); a closely agreeing value is given by *E.M.F.* measurements. The solubility of picric acid in water at 25° is c_0=0·0575 mol. per litre, and its solubility has been measured in aqueous solutions of sodium chloride, barium chloride, and magnesium sulphate. The partition of picric acid between benzene and aqueous solutions of the above-mentioned salts has also been studied, and the hydrogen-ion concentration calculated in each case. The experimental results together with those of Rothmund and Drucker (A., 1904, ii, 391) are used to calculate the partition and solubility constants on the basis of Bjerrum's theory, and satisfactorily constant values are obtained. W. H.-R.

Steric Hindrance in the Migration of Acyl from Nitrogen to Oxygen. L. C. RAIFORD and C. M. WOOLFOLK (*J. Amer. Chem. Soc.*, 1924, **46**, 2246—2255).—The migration of the acetyl group from nitrogen to oxygen when an *o*-acetamidophenol is benzoylated by the Schotten–Baumann method (A., 1923, i, 326) is not inhibited by the presence of bromine atoms ortho to the amino and hydroxyl groups, although in the case of 2 : 5 : 6-tribromo-3-acetamido-*p*-cresol either benzoylation was incomplete or migration was only partial.

2 : 3 : 5-Tribromo-*p*-cresol, m. p. 99°, on treatment with sodium nitrite and glacial acetic acid, is converted into 2 : 5-dibromo-3-nitro-*p*-cresol (or 5 : 6-dibromo-3-nitro-*p*-cresol), m. p. 123°, which is reduced by Raiford's method (A., 1911, i, 993) to the corresponding 2 : 5(or 5 : 6)-dibromo-3-amino-*p*-cresol, m. p. 122°.

Acetic anhydride and sodium acetate convert the base into 2 : 5 (or 5 : 6)-*dibromo*-3-*acetamido*-p-*tolyl acetate*, needles, hydrolysed by 10% aqueous sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo*-3-*acetamido*-p-*cresol*, m. p. 158°, which with benzoyl chloride and sodium hydroxide gives, in 77% yield, 2 : 5(or 5 : 6)-*dibromo*-3-*benzoylamido*-p-*tolyl acetate*, m. p. 232°, hydrolysed by methyl-alcoholic sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo*-3-*benzoyl-amido*-p-*cresol*, m. p. 154° (decomp.). The latter compound is identical with that obtained by benzoylating 2 : 5(or 5 : 6)-dibromo-3-amino-*p*-cresol by Ransom's method (A., i, 1900, 218) and on acetylation is converted into the benzoylamido-*p*-tolyl acetate.

Acetylation of 2 : 5 : 6-*tribromo*-3-*amino*-p-*cresol* with sodium acetate and acetic anhydride gives in 92% yield slightly impure 2 : 5 : 6-*tribromo*-3-*acetamido*-p-*tolyl acetate*, m. p. 171°, which on hydrolysis with 1% sodium hydroxide yields 2 : 5 : 6-*tribromo*-3-*acetamido*-p-*cresol*, m. p. 189°. Benzoyl chloride and sodium hydroxide convert this into 2 : 5 : 6-*tribromo*-3-*benzoylamido*-p-*tolyl acetate*, m. p. 177° (blackening) (yield 72%), the structure of which follows from its hydrolysis with aqueous alcoholic sodium hydroxide to 2 : 5 : 6-*tribromo*-3-*benzoylamido*-p-*cresol*, m. p. 195°, identical with the product obtained by benzoylating 2 : 5 : 6-tribromo-3-amino-*p*-cresol by Ransom's method. Acetic anhydride and sodium acetate convert the benzoylamido-*p*-cresol into the *p*-tolyl acetate, m. p. 195°.

Tetrabromo-*o*-cresol, m. p. 204°, on treatment with sodium nitrite and acetic acid, gives in addition to the 4 : 5 : 6-tribromo-3-nitro-*o*-cresol, m. p. 159°, the isomeric 3 : 4 : 6-tribromo-5-nitro-*o*-cresol, m. p. 177° (decomp.), obtained by Zincke and Klostermann (A., 1907, i, 322). On reduction by Raiford's method, the 4 : 5 : 6-tribromo derivative gives, in 74% yield, the *hydrochloride* of 4 : 5 : 6-*tribromo*-3-*amino*-o-*cresol*; the free *base* has m. p. 167°. Acetylation of the base by the usual method gives, in 86% yield, 4 : 5 : 6-*tribromo*-3-*acetamido*-o-*tolyl acetate*, m. p. 146°, which on hydrolysis with aqueous alcoholic alkali gives an 82% yield of 4 : 5 : 6-*tribromo*-3-*acetamido*-o-*cresol*, m. p. 186°. Benzoylation converts the last into 4 : 5 : 6-*tribromo*-3-*benzoylamido*-o-*tolyl acetate*, m. p. 234°, the structure of which is established by its synthesis by benzoylation of 4 : 5 : 6-tribromo-3-amino-*o*-cresol by Ransom's method, followed by acetylation of the 4 : 5 : 6-*tribromo*-3-*benzoylamido*-o-*cresol*, m. p. 133°, with sodium acetate and acetic anhydride. R. B.

Influence of Weight of Acyl in the Migration from Nitrogen to Oxygen. II. L. C. Raiford amd J. R. Couture (*J. Amer. Chem. Soc.*, 1924, **46**, 2305—2318).—In continuation of their previous work on the migration of acetyl from nitrogen to oxygen in benzoylation by the Schotten–Baumann method (A., 1920, i, 156; 1922, i, 931; 1923, i, 326, 925), the authors have repeated the work of Auwers and Eisenlohr on acetylbenzoyl derivatives of 3-amino-*p*-cresol. Two different mixed diacyl derivatives were obtained, each of which gave a mixture of mono-*N*-acylated derivatives on hydrolysis. A study of the acylation of 5-bromo-3-amino-*p*-cresol

and 4 : 6-dibromo-*o*-aminophenol shows that an increase in the weight of the aliphatic acyl radical hinders its displacement by benzoyl. The introduction of a nitro group into the benzoyl radical in the meta- or para-position greatly weakens the power of the radical to displace other groups from nitrogen in acylated *o*-aminophenols. The effect is greatest when the nitro group is in the para-position, but the introduction of a chlorine atom in the para-position does not diminish the power of the benzoyl group to displace other acyl groups. Neither relative weight nor relative acidity of the acyl radicals is the sole determining factor in the migration, and rearrangement may occur in both directions either in acylation or in hydrolysis. With two acyl groups of the same weight, one aromatic and one aliphatic, there is little tendency for replacement in acylation, but migration may occur during hydrolysis.

3-Acetamido-*p*-cresol, m. p. 158°, on benzoylation, yields 3-acetamido-*p*-tolyl benzoate, m. p. 147°; the isomeric 3-benzamido-*p*-tolyl acetate melts at 135°. 4 : 6-*Dibromo*-o-*propionamidophenyl propionate*, m. p. 162°, obtained on heating the hydrochloride of the base with sodium propionate and excess of propionic anhydride [the *tripropionyl* derivative, $C_3H_5O{\cdot}OC_6H_2Br_2{\cdot}N(C_3H_5O)_2$, m. p. 153°, is obtained with a large excess of anhydride], on hydrolysis with dilute alkali yields 4 : 6-*dibromo*-o-*propionamidophenol*, m. p. 88°, which on benzoylation gives in 99·4% a *propionylbenzoyl* derivative, m. p. 182°, identical with that obtained by the action of propionic anhydride on 4 : 6-dibromo-*o*-benzoylamidophenol, and yielding on hydrolysis a mixture of the *N*-benzoyl and *N*-propionyl compounds. 4 : 6-*Dibromo*-o-n-*hexoamidophenyl hexoate*, m. p. 111°, obtained by the action of *n*-hexoyl chloride on the phenol in pyridine, on hydrolysis yields 4 : 6-*dibromo*-o-*hexoamidophenol*, m. p. 70—71°, converted quantitatively by benzoyl chloride into 4 : 6-*dibromo*-o-*hexoamidophenyl benzoate*, m. p. 137°, hydrolysed to a mixture of *N*-benzoyl and *N*-hexoyl-4 : 6-dibromo-*o*-aminophenol. The isomeric 4 : 6-*dibromo*-o-*benzoylamidophenyl hexoate*, m. p. 137°, also yields a mixture of the two *N*-acyl derivatives on hydrolysis. Similarly, 4 : 6-*dibromo*-o-*acetamidophenyl hexoate*, m. p. 120°, obtained by the action of hexoyl chloride on *o*-acetamidophenol, and 4 : 6-*dibromo*-o-*hexoamidophenyl acetate*, m. p. 133°, similarly prepared from *o*-hexoamidophenol, both yield on hydrolysis a mixture of the two acylamidophenols. Acetylation of 5-bromo-3-amino-*p*-cresol with excess of acetic anhydride in pyridine gives a *triacetyl* derivative, m. p. 109°, $OAc{\cdot}C_6H_2Br(Me){\cdot}NAc_2$. The diacetyl derivative obtained with acetyl chloride yields on hydrolysis the *N*-acetyl derivative, which with *p*-nitrobenzoyl chloride in pyridine is quantitatively converted into 5-*bromo*-3-*acetamido*-p-*tolyl* p-*nitrobenzoate*, m. p. 206°, identical with the product obtained by the action of acetyl chloride on 5-*bromo*-3-p-*nitrobenzoylamido*-p-*cresol*, m. p. 190°, and yielding *p*-nitrobenzoic acid and the acetamidophenol on hydrolysis. *p*-Nitrobenzoyl chloride and 4 : 6-dibromo-*o*-benzoylamidophenol, and benzoyl chloride and 4 : 6-*dibromo*-p-*nitrobenzoylamidophenol*, m. p. 214°, obtained by hydrolysis of the diacyl compound, yield the same *benzoylnitrobenzoyl* derivative, m. p.

246°, which on hydrolysis yields *p*-nitrobenzoic acid and the benzoylamidophenol. Similarly, the same *acetyl*-m-*nitrobenzoyl* compound, m. p. 190°, was obtained by the action of *m*-nitrobenzoyl chloride on 5-bromo-3-acetamido-*p*-cresol and of acetyl chloride on 5-*bromo*-3-m-*nitrobenzoylamido*-p-*cresol*, m. p. 190°, the diacyl compound on hydrolysis yielding both possible acylaminophenols. 5-*Bromo*-3-p-*chlorobenzoylamido*-p-*cresol*, m. p. 166°, from hydrolysis of the diacyl derivative, with acetyl chloride, and 5-bromo-3-acetamido-*p*-cresol with *p*-chlorobenzoyl chloride, yield the same diacyl derivative, which on hydrolysis yields the *N*-*p*-chlorobenzoyl derivative, but no *p*-chlorobenzoic acid. Similarly, 4 : 6-*dibromo*-2-p-*chlorobenzoylamidophenol*, m. p. 209—210°, and *p*-nitrobenzoyl chloride yield a p-*chlorobenzoyl*-p-*nitrobenzoyl* derivative, m. p. 276°, identical with that obtained from 4 : 6-dibromo-2-*p*-nitrobenzoylamidophenol and *p*-chlorobenzoyl chloride. On hydrolysis, this yields only *p*-nitrobenzoic acid and the *N*-*p*-chlorobenzoyl derivative, m. p. 209—210°. R. B.

Nitration of Derivatives of *p*- and *m*-Aminophenols. F. Reverdin (*Bull. Soc. chim.*, **1924**, [iv], **35**, 1168—1183).—A general survey of researches on the nitration of derivatives of *p*-aminophenol (A., 1905, i, 51, 430; 1906, i, 165, 748; 1907, i, 37, 695; 1909, i, 377, 913; 1910, i, 470; 1911, i, 37, 776; 1912, i, 182, 963; 1913, i, 850; 1922, i, 537; 1923, i, 320, 714; this vol., i, 727) and *m*-aminophenol (A., 1914, i, 166, 831, 954; 1915, i, 60, 524, 878; 1916, i, 141, 645). R. B.

Action of Formic Acid on Phenols and Propenyl Phenolic Ethers. L. S. Glichitch (*Bull. Soc. chim.*, 1924, [iv], **35**, 1160—1164).—Phenolic ethers containing a propenyl side-chain are converted by boiling with 90% formic acid into their dimeric forms, which are thus readily obtained pure (cf. Semmler, A., 1908, i, 664). Anethole is converted in this way into dianethole, m. p. 133·5—134° (cf. Orndorff, A., 1898, i, 129), *iso*eugenol into di*iso*eugenol, methyl-*iso*eugenol into dimethyldi*iso*eugenol, m. p. 105·5—106° (cf. Széki, A., 1906, i, 660; Ciamician and Silber, A., 1909, i, 306), *iso*safrole into di*iso*safrole, m. p. 145—145·5°, whilst the isomeric allyl compounds, methylchavicol, eugenol, methyleugenol, and safrole, are unchanged. The crude dimethyldi*iso*eugenol melts at 89°, but no compound m. p. 96° could be isolated in the recrystallisations. R. B.

Pyrocatechol Compounds of Sexa- and Quinque-valent Molybdenum. R. Weinland and P. Huthmann (*Arch. Pharm.*, 1924, **262**, 329—343; cf. A., 1920, i, 40).—Among the compounds of pyrocatechol and molybdic acid are many containing one or two pyrocatechol residues per atom of molybdenum, viz.,

$$MoO_2(OH)\cdot O\cdot C_6H_4\cdot OX$$

and $MoO_2(O\cdot C_6H_4\cdot OX)_2$, (where $X=NH_4$ or an organic basic radical). It is possible to obtain a number of products containing a higher proportion of pyrocatechol, but it is now shown that in these only two pyrocatechol residues are attached to the molybdenum,

forming a complex anion, the rest of the pyrocatechol being probably attached to the cation by a secondary valency. If the compounds with organic bases having more than two pyrocatechol residues per atom of molybdenum are recrystallised, they readily lose some of their pyrocatechol and finally a compound is obtained containing never less than two pyrocatechol residues. Ethylenediamine forms such a compound, containing five pyrocatechol residues, and three of these may be readily removed as above. Pyrocatechol compounds of quinquevalent molybdenum are all prepared from the green salt, $MoOCl_3,2NH_4Cl$. As this gives a hydroxide, $MoO(OH)_3$, it was expected that it would yield compounds with three pyrocatechol residues per atom of molybdenum, but none was obtained with more than two. The following new substances are described: *barium monopyrocatecholmolybdate*, $[MoO_3(O{\cdot}C_6H_4{\cdot}O)]_2H_2Ba,3H_2O$, prepared from the corresponding ammonium salt; the *mono-* and *di-guanidine* salts (which, like the other members of this series, may be prepared by the interaction of either ammonium molybdate or the trioxide MoO_3, pyrocatechol, and the appropriate base or its salts), $[MoO_3(O{\cdot}C_6H_4{\cdot}O)]H_2{\cdot}CH_5N_3$, and

$$[MoO_2(O{\cdot}C_6H_4{\cdot}O)_2]H_2(CH_5N_3)_2,C_6H_4(OH)_2;$$

the *ethylenediamine* salt,

$$[MoO_2(O{\cdot}C_6H_4{\cdot}O)_2]H_2,C_2H_8N_2,3C_6H_4(OH)_2,H_2O,$$

the *piperidine* salts, $2[MoO_3(O{\cdot}C_6H_4{\cdot}O)]H_2{\cdot}C_5H_{11}N,3H_2O$ and $[MoO_2(O{\cdot}C_6H_4{\cdot}O)_2]H_2(NH_3){\cdot}(C_5H_{11}N),2H_2O$; the *piperazine* salts, $[MoO_2(O{\cdot}C_6H_4{\cdot}O)_2]H_2{\cdot}C_4H_{10}N_2$ (and its mono- and di-hydrates) and $[MoO_3(O{\cdot}C_6H_4{\cdot}O),MoO_2(O{\cdot}C_6H_4{\cdot}O)_2]H_4{\cdot}C_4H_{10}N_2,2H_2O$ (and the corresponding tetrahydrate). The following derivatives of quinquevalent molybdenum are described: *guanidine* salt,

$$[MoO_2(O{\cdot}C_6H_4{\cdot}O)(OH)]H_2{\cdot}(CH_5N_3)_2,1\tfrac{1}{2}H_2O;$$

pyridine salt,

$$[MoO_2(O{\cdot}C_6H_4{\cdot}O)(OH),MoO(O{\cdot}C_6H_4{\cdot}O)_2(OH)]H_4{\cdot}(C_5H_5N)_2;$$

piperazine salt, $[MoO(O{\cdot}C_6H_4{\cdot}O)_2(OH)]H_2{\cdot}C_4H_{10}N_2,H_2O$. B. F.

Preparation of Potassium Guaiacolsulphonate ("Thiocol"). A. Decio (*Boll. Chim. farm.*, 1924, **63**, 529—530).—Guaiacolsulphonic acid, prepared by the action of sulphuric acid on guaiacol, is converted, together with the excess of sulphuric acid, into calcium salt by neutralisation with calcium carbonate. Treatment of the mixed calcium salts with potassium carbonate converts the calcium guaiacolsulphonate into the corresponding potassium salt, the calcium carbonate formed and the calcium sulphate being then removed by filtration. [Cf. *B.*, 1924, 964.] T. H. P.

Electrolytic Introduction of Alkyl Groups. J. M. Nelson and A. M. Collins (*J. Amer. Chem. Soc.*, 1924, **46**, 2256—2267).—In the electrolysis of a mixture of benzaldehyde and ethyl iodide, saturated with tetraethylammonium iodide, *α-phenylpropyl ethyl ether*, CHPhEt·OEt, b. p. 85—90°/15 mm., having a characteristic, pleasant odour, is obtained. It is oxidised to propiophenone by potassium dichromate and sulphuric acid. The introduction of the two ethyl groups is analogous to the reduction of benzalde-

hyde to benzyl alcohol and to its conversion into α-phenylpropyl alcohol by the Grignard reaction. The introduction of alkyl groups appears to take place with difficulty and other reactions occur simultaneously. Part of the benzaldehyde undergoes reduction to *as*-diphenylethylene glycol, *s*-diphenylethylene glycol (hydrobenzoin), and stilbene, which, together with ethylene, a benzoate resembling ethyl benzoate, an iodide (giving with dimethylaniline a substance, m. p. 152°) similar to, but not identical with, benzyl iodide, and a residual tar, are all formed at the cathode. Hydrobenzoin is always formed even when benzoic acid and water are excluded and the electrolysis is conducted in an atmosphere of nitrogen, and its formation may possibly take place as indicated: $2CHPhO+2EtI+2e \longrightarrow [CHPh(OH)\cdot]_2+2C_2H_4+2I^-$, a reaction which is analogous to the reducing action of magnesium ethyl bromide (cf. Hess and Rheinboldt, A., 1921, i, 777). The yield of α-phenylpropyl ethyl ether is not affected by the presence of traces of benzoic acid, nor by the absence of a diaphragm.

Preliminary experiments with benzaldehyde and methyl iodide indicate that a similar reaction obtains in this case, an *ether* which on oxidation yields acetophenone, and is probably α-phenylethyl methyl ether, being obtained. Attempts to introduce methyl groups into benzonitrile, propionitrile, and acetone by this method were unsuccessful, methane being formed practically in quantitative yield, calculated on the current consumption. R. B.

Utilisation of Cassia Oil for the Synthesis of Cinnamyl Alcohol. A. J. Hill and E. H. Nason (*J. Amer. Chem. Soc.*, 1924, **46**, 2236—2246).—The sodium hydrogen sulphite method of separating cinnamaldehyde from cassia oil is unsuitable for large-scale working (cf. Heusler, A., 1891, 1052; Tiemann, A., 1898, i, 247), but 85·7% of the theoretical yield can be separated as cinnamylidene diacetate by treatment of the oil with acetic anhydride in the presence of a few drops of sulphuric acid. The diacetate is readily hydrolysed to the aldehyde by heating with 10% sulphuric acid (yield 96%). On reduction of the diacetate with iron (8·3 mols.) and 50% acetic acid, yields of cinnamyl acetate up to 63·7% of theory (cf. Barbier and Leser, A., 1905, i, 653) are obtained in 12 hours. Large amounts of acetic acid retard the reduction. Copper sulphate inhibits the reduction, whilst nickel sulphate promotes the formation of phenylpropyl alcohol. With aluminium amalgam, reduction is incomplete; zinc–copper and zinc–nickel couples in alcoholic solution give hydrocinnamoin and other glycols (cf. Thiele, A., 1899, i, 616). Reduction with zinc and acetic acid gives similar results, cinnamyl acetate never being obtained when zinc is used. Cinnamyl acetate can also be obtained by reduction of cinnamaldehyde or cassia oil by the same method, the yield in the latter case being 77% of theory. Hydrolysis of the acetate with 5% alcoholic sodium hydroxide gives 96% of the theoretical yield of cinnamyl alcohol (p-*nitrobenzoate*, m. p. 78°), which is separated from any phenylpropyl alcohol by treatment with calcium chloride, with which the cinnamyl alcohol

forms an additive compound. Cinnamaldehyde is best determined by precipitation of the phenylhydrazone in glacial acetic acid.

R. B.

Molecular Transformations. XIV. Action of Acetyl Chloride on 4 : 4′ : 4″ : 4‴-Tetrabromobenzopinacone. Contribution to the Problem of Affinity. P. J. MONTAGNE (*Rec. trav. chim.*, 1924, **43**, 636—642; cf. *Ber.*, 1918, **51**, 1479).—The action of acetyl chloride on 4 : 4′ : 4″ : 4‴-tetrabromobenzopinacone simultaneously follows two courses. The main reaction results in the formation of 4 : 4′ : 4″ : 4‴-tetrabromobenzopinacolin, whilst the side reaction gives 4 : 4′-dibromobenzhydrol. This is explained by assuming that in acetyl chloride solution two forms of the tetrabromobenzopinacone are present in mutual equilibrium. The difference between the forms lies in the distribution of affinity between the atoms of the molecule. Which of the two changes, intramolecular transformation or decomposition, a particular molecule undergoes is determined by the relative intensities of its main and subsidiary valencies. According to this theory, in the pinacone–pinacolin transformation, the elimination of water and the migration of the bromophenyl group take place simultaneously.

W. E. E.

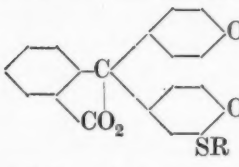
2-Hydroxy-5-methoxy*cyclo*hexylcarbinol. L. HELFER (*Helv. Chim. Acta*, 1924, **7**, 950—956).—*p*-Hydroxyanisole is hydrogenated in the presence of reduced nickel to 4-*methoxy*cyclo*hexanol*, b. p. 204—205° (*acetyl* derivative, b. p. 102—103°/12 mm.). Oxidation by potassium dichromate and sulphuric acid leads to 4-*methoxy*cyclo*hexanone* (b. p. 200—201°/760 mm., 72°/9 mm.; semicarbazone, m. p. 178°), which gives, with sodium ethoxide and *iso*amyl formate, 4-*methoxy*-2-*hydroxymethylene*cyclo*hexanone* (b. p. 108—110°/10 mm.). Sodium and alcohol reduce this to 6-*hydroxy*-3-*methoxy*cyclo*hexylcarbinol*, b. p. 172—174°/13 mm. 2-Hydroxymethylene-4-methyl*cyclo*hexanone gives with semicarbazide a cyclic semicarbazone, $\begin{matrix}CH_2—CH_2—C=N\\ |\qquad\qquad |\\ CHMe\cdot CH_2\cdot C\cdot CH\end{matrix}\!>\!N\cdot CO\cdot NH_2$, m. p. 161°. It is reduced in the same way as the corresponding methoxy compound (above) to 2-*hydroxy*-5-*methyl*cyclo*hexylcarbinol*, m. p. 70°. The action of formaldehyde on *p*-hydroxyanisole in the presence of calcium hydroxide gives 2-*hydroxy*-5-*methoxybenzyl alcohol* (m. p. 81°) and a little 2-*hydroxy*-5-*methoxy*-m-*xylylene glycol*, m. p. 127°.

W. E. E.

Effect of Sulphur on the Colour of certain Phthaleins. H. S. HOLT and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 2333—2337).—By condensing *p*-hydroxybenzoyl-*o*-benzoic acid with *o*-hydroxyphenyl thio-ethers in the presence of zinc chloride (cf. Orndorff and Murray, A., 1917, i, 339), a series of derivatives of phenolphthalein containing the alkylthiol (or alkylsulphone) group ortho to hydroxyl has been obtained. The products form oximes, acetates, and benzoates, but the acetates could not be crystallised or the benzoates purified. The introduction of the methylthiol

group changes the colour of the phenolphthalein in alkaline solution to purple, but the auxochrome effect diminishes with increasing weight of the alkyl group. The phenylthiol group has practically no effect and the methylsulphone group none. The p_H value of the indicator is only slightly affected. Similar products were obtained by condensing *p*-hydroxybenzoyl-*o*-benzoic acid with phenyl mercaptan, *o*-nitrophenyl mercaptan, *p*-nitrophenyl methyl sulphide, and *o*-nitrophenyl methyl sulphide, but were not purified.

The following thio-ethers were obtained by diazotisation of the corresponding *o*-amino derivative: o-*hydroxyphenyl methyl sulphide*, b. p. 105°/22 mm., d_{25}^{25} 1·168; o-*hydroxyphenyl amyl sulphide*, b. p. 125°/10 mm., d_{25}^{25} 1·061; *phenyl* o-*hydroxyphenyl sulphide*, m. p. 44°, and o-*hydroxyphenylmethylsulphone*, m. p. above 220°. The following ethers of 3-*thiolphenolphthalein* (annexed formula) have been obtained: *methyl*, p_H 8·4—10, *oxime*, m. p. 189° (decomp.); *amyl*, p_H 8·6—9·8, *oxime*, m. p. 175—176° (decomp.); *phenyl*, p_H 9·0—10, *oxime*, m. p. 190° (decomp.).



4 : 4′-*Dihydroxydiphenylphthalide*-3-*methylsulphone* has p_H 9·6, *oxime*, m. p. 165—167° (decomp.). Fusion of phthalic anhydride (1 mol.) with *o*-hydroxyphenyl methyl sulphide (2 mols.) and zinc chloride at 180° yields a salmon-coloured *hydroxymethylthiolanthraquinone*, m. p. 188° (decomp.).

R. B.

Diacylamides. I. K. Brunner, W. Seeger, and S. Dittrich (*Monatsh.*, 1924, **45**, 69—86; cf. Brunner, A., 1915, i, 1007; Miller, A., 1916, i, 203; Wolchowe, A., 1916, i, 844).—Diacylamides react with secondary hydrazines and aromatic amines to give substituted hydrazidines and amidines, respectively, in addition to acetylated derivatives, thus resembling nitriles. Diacetamide and *as*-phenylmethylhydrazine (equivalent quantities) were digested in 10% acetic acid at 100° for 24 hours; the fraction, b. p. 160—185°/13—17 mm., was freed from much acetylated hydrazine by crystallisation and the residue converted by ethereal oxalic acid into the *oxalate* of acetophenylmethylhydrazidine, m. p. 129—130°. Treatment with barium hydroxide gave the *base*,

$$NMePh\cdot NH\cdot CMe{:}NH,$$

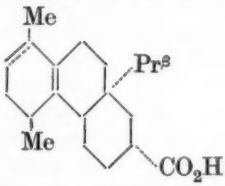
m. p. 83—84° (yield 7%); *picrate*, m. p. 158—159°; *dibenzoyl* derivative, m. p. 148—149°; *methiodide*, m. p. 210° (decomp.).

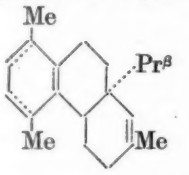
Dibenzamide and aniline do not condense in presence of sodium (cf. Walther, A., 1894, i, 503; Lottermoser, A., 1897, i, 38), but by heating equivalent amounts of the amide and aniline hydrochloride at 140—145° benzphenylamidine, m. p. 113·5°, is formed in 10% yield, together with benzanilide and benzamide from a by-reaction, and benzoic acid. The hydrochloride, m. p. 224°, and chloroplatinate are described. The reaction does not depend on the formation of benzonitrile, which does not react with aniline hydrochloride at so low a temperature. Dibenzamide does not react similarly with dimethylaniline hydrochloride, but with

diphenylaniline hydrochloride at 170° it gives benzdiphenylamidine, $CPh(:NH)\cdot NPh_2$, m. p. 112°. F. M. H.

Higher Terpene Compounds. XXIII. *d*-Pimaric Acid. L. RUZICKA and F. BALAS (*Helv. Chim. Acta*, 1924, **7**, 875—885; cf. A., 1923, i, 818).—When *d*-pimaric acid is dehydrogenated by means of sulphur, it gives a dimethylphenanthrene, $C_{16}H_{14}$; it loses not only a carboxyl group, but also three other carbon atoms, which are taken to represent a tertiary *iso*propyl group. Together with the evidence of molecular refraction, this result leads to the conclusion that *d*-pimaric acid is probably a dimethyl*iso*propyldecahydrophenanthrenecarboxylic acid. When dehydrogenated by means of sulphur, ethyl *d*-pimarate gives the same product as the acid itself. In order to locate the carboxyl group, ethyl *d*-pimarate is reduced to d-*pimarol*, $C_{20}H_{32}O$, b. p. 166—168°/0·1 mm., d_4^{15} 1·0114, n_D^{15} 1·5357, from which, by elimination of water, *methyl*-d-*pimarin*, $C_{20}H_{30}$, b. p. 140—145°/0·3 mm., d_4^{23} 0·9587, n_D^{23} 1·5301, is obtained. Dehydrogenation of this compound by means of sulphur gives a new *trimethylphenanthrene*, $C_{17}H_{16}$, m. p. 81° (*picrate*, m. p. 115°; *quinone*, m. p. 154°; *quinoxaline*, m. p. 154°), in which the methyl group derived from the carboxyl group of *d*-pimaric acid is still present. Hence this methyl group, and therefore the original carboxyl group, cannot be tertiary. This result is also to be expected from the difficulty with which *d*-pimaric acid is esterified. The trimethylphenanthrene from methyl-*d*-pimarin oxidises to a quinone of the same number of carbon atoms, therefore in *d*-pimaric acid positions 9 and 10 of the phenanthrene nucleus are vacant. The subjoined formula I is accordingly proposed for *d*-pimaric acid.

(I.)





(II.)

When *d*-pimaric acid is converted into methyl-*d*-pimarin, a third double bond, adjacent to the carboxyl group, is produced. But methyl-*d*-pimarin is highly unsaturated, and it follows that the two double bonds of *d*-pimaric acid cannot be in the same ring as the carboxyl group. On the other hand, dehydrogenation with nickel and palladium introduces only one more double bond into methyl-*d*-pimarin, forming *dehydromethyl*-d-*pimarin*, $C_{20}H_{28}$, b. p. 185—195°/12 mm., d_4^{14} 0·9771, n_D^{14} 1·5404 (formula II). This is explained if the double bonds of *d*-pimaric acid are as shown in I; the tertiary *iso*propyl group common to the two rings prevents their dehydrogenation. That there is probably no double bond adjacent to the carboxyl group of *d*-pimaric acid follows from the fact that the Bouveault reduction of simple αβ-unsaturated esters always leads to a saturated product. When *d*-pimaryl chloride is distilled in a vacuum, d-*pimarin*, $C_{19}H_{28}$, b. p. 182—184°/12 mm., $[\alpha]_D$ +109°, d_4^{15} 0·9693, n_D^{15} 1·5349, is obtained. This compound contains

three double bonds, and the fact that it is unsaturated supports the former conclusion that the two double bonds of *d*-pimaric acid are not in the same ring as the carboxyl group. The partial dehydrogenation of *d*-pimarin gives *dehydro*-d-*pimarin*, $C_{19}H_{26}$, b. p. 203—212°/12 mm., d_4^{15} 0·9863, n_D^{15} 1·5505, which is notably less unsaturated than *d*-pimarin. This is further support for the structure of *d*-pimaric acid given, since dehydro-*d*-pimarin, like its higher homologue, II, contains a benzene nucleus. d-*Pimarin*, obtained by heating *d*-pimaric acid at 310°, has b. p. 184—186°/12 mm., $[\alpha]_D$ +30·1° in 4% chloroform solution, d_4^{23} 0·9717, n_D^{23} 1·5406. W. E. E.

Derivatives of Hexamethylenetetramine. Gehe u. Co. A.-G., and H. Runne (D.R.-P. 386691; from *Chem. Zentr.*, 1924, i, 2612).—By combining aryloxyacetic acids with hexamethylenetetramine, the bitter taste of the acids is neutralised, the salts having a slightly sweet after-taste; they are useful as internal or external antiseptics. The following salts, prepared in the usual way, are described: *phenoxyacetate*, sinters about 177°; p-*tolyloxyacetate*, sintering about 194°; *guaiacolglycollate*, sintering about 130°; *salicyloxyacetate* (1 mol. acid +2 mols. base), sintering about 86°; *acid salicyloxyacetate* (1 mol. acid +1 mol. base) crystallises slowly and is more hygroscopic than the neutral salt. F. A. M.

Halogenated Anhydrides of *o*-Hydrocoumaric Acid [Melilotic Acid]. Chemische Werke Grenzach A.-G. (D.R.-P. 386619; from *Chem. Zentr.*, 1924, i, 2633).—Halogenated coumarins or halogenated *o*-coumaric acids are treated with reducing agents and the resulting halogenated *o*-hydrocoumaric acids converted into the anhydrides by heating. 3 : 5-*Dichlorocoumarin*, m. p. 157° (from 3 : 5-dichlorosalicylaldehyde) on reduction with sodium amalgam in aqueous suspension yields 3 : 5-*dichloromelilotic acid*, m. p. 122°, which on heating at 210° gives the *anhydride*, m. p. 107°, b. p. 204°/25 mm. 5-*Chlorocoumarin* (from 5-chlorosalicylaldehyde), m. p. 165°, is reduced by sodium amalgam to 5-chloromelilotic acid, m. p. 142°, giving the anhydride, m. p. 109°, b. p. 192°/20 mm. The anhydrides are of value against intestinal parasites. F. A. M.

Elemic Acid from Manila Elemi Resin. H. Lieb and D. Schwarzl (*Monatsh.*, 1924, **45**, 51—61).—To α-elemic acid from *Canarium commune* is assigned the formula $C_{27}H_{42}O_3$ (contrast Tschirch and Cremer, A., 1902, i, 812; Buri, A., 1878, ii, 439); it is transformed by light into a resin which is regarded as identical with Tschirch and Cremer's β-acid.

α-Elemic acid, m. p. 215°, is a monocarboxylic acid; $[\alpha]_D^{19}$ −24·48° in alcohol. There are described: *potassium* salt (+$5H_2O$), becoming anhydrous at 115°, hydrolysed by water; *sodium* salt (+$5H_2O$); amorphous *silver* salt, which with methyl iodide gives the *monomethyl* ester (gummy). Tschirch and Cremer's preparation of an acetyl and benzoyl derivative could not be repeated.

Oxidation of α-elemic acid with chromic oxide in acetic acid gave a monocarboxylic *acid*, $C_{27}H_{40}O_3$, m. p. 274°, $[\alpha]_D^{13}$ −67·13°

in chloroform; *sodium* salt ($+7H_2O$). Although attempts to prepare a crystalline oxime, semicarbazone, or hydrazone were unsuccessful, it is regarded as a ketonic acid, and the name "elemonic acid" is suggested for it; α-elemic acid must then contain a secondary alcoholic group, and for it is suggested the name "elemolic acid." Both readily take up bromine, whilst subsequent elimination of hydrogen bromide leaves an amorphous residue.

Oxidation of α-elemic acid with nitric acid gave an amorphous acid, $C_{21}H_{25}O_{10}N_3$ (cf. Tschirch and Cremer, *loc. cit.*), decomp. 175°; *silver* salt, $C_{21}H_{23}O_{10}N_3Ag_2$. [Cf. *B.*, 1924, 952.]

F. M. H.

Ring-chain Tautomerism. X. Inhibited Tautomerism. F. Dickens, L. Horton, and J. F. Thorpe (*J. Chem. Soc.*, 1924, **125**, 1830—1840).—From *cyclo*hexanone cyanohydrin (Higson and Thorpe, T., 1906, **89**, 1455) and ethyl sodiocyanoacetate, *ethyl* 1-*cyano*cyclo*hexane*-1-*cyanoacetate*, m. p. 54°, b. p. 210—212°/22 mm., is obtained. When hydrolysed, it affords 1-carboxy*cyclo*hexane-1-acetic acid. The sodium derivative of the ester decomposes when its solution is evaporated, yielding 1-*cyano*cyclo*hexane*-1-*acetonitrile*, m. p. 84°, and *sodium* 1-*cyano*cyclo*hexane*-1-*cyanoacetate*, m. p. 145—149° (*silver* and *aniline* salt [m. p. 98°] also described). When a solution of this sodium salt (which is the main product when a small excess of sodium is used in the hydrolysis) is acidified and the oily precipitate first formed redissolved in an excess of hydrochloric acid, 1-*carbamyl*cyclo*hexane*-1-*cyanoacetic acid*, m. p. 90° (decomp. 100°), crystallises (*sodium* salt, m. p. 105—108°). When heated at 72—74° this acid affords ammonium 1-carboxy*cyclo*hexane-1-acetate, together with the *imide* of α-*carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 152° (decomp.); when it is treated with acetic acid, the *imide* of 1-*carboxy*cyclo*hexane*-1-*cyanoacetic acid*, m. p. 123—124°, is obtained, and this, when boiled with aqueous potassium hydroxide, affords α-*carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 126°, which is converted at its melting point into the *imide* of 1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 145° (this is also obtained by interaction of 1-carboxy-*cyclo*hexane-1-acetic anhydride and carbamide). When 1-cyano-*cyclo*hexane-1-acetonitrile is dissolved in concentrated sulphuric acid, it is converted into 1-*carbamyl*cyclo*hexane*-1-*acetamide*, m. p. 201°.

When the sodium compound of ethyl αβ-dicyano-ββ-dimethylpropionate (Higson and Thorpe, *loc. cit.*) is treated with water it affords a mixture of (i) *as*-dimethylsuccinonitrile, m. p. 68° (this is best prepared by boiling the solution and is not a liquid as stated by Hell and Lothberg [A., 1889, 959]); (ii) the *imide* of α-*cyano*-ββ-*dimethylsuccinic acid*, m. p. 116°, and (iii) β-*carbamyl*-α-*cyano*-ββ-*dimethylpropionic acid*, m. p. 142°. The first is converted by cold concentrated sulphuric acid into as-*dimethylsuccinamide*, m. p. 153°, and (iii) is converted into (ii) by hot acetic acid.

*cyclo*Heptanone cyanohydrin condenses with ethyl sodiocyanoacetate to give *ethyl* 1-*cyano*cyclo*heptane*-1-*cyanoacetate*, b. p.

201°/13 mm., the sodium compound of which, when treated with water and the solution evaporated to dryness, yields the corresponding sodium salt. The free acid cannot be obtained; a solution of the sodium salt yields when acidified solely the *imide* of 1-*carboxy*cyclo*heptane*-1-*cyanoacetic acid*, m. p. 130°. The sodium salt is accompanied by some 1-*cyano*cyclo*heptane*-1-*acetonitrile*, m. p. 58°. When ethyl 1-cyano*cyclo*heptane-1-cyanoacetate is dissolved in concentrated sulphuric acid and the diluted solution boiled, the *imide* of 1-*carboxy*cyclo*heptane*-1-*acetic acid*, m. p. 116°, is formed, together with a little 1-*carboxy*cyclo*heptane*-1-*acetic acid*, m. p. 153°.

The parent compounds of all three series are ββ-disubstituted αβ-dicyanopropionic acids; the mechanism of the various reactions is discussed on the lines indicated by the title of the paper, the effect of the different modes of ββ-substitution on the proximity of the other groups being kept in view. W. A. S.

Isomeric Esters of *p*-Ethoxybenzoylacrylic Acid. G. P. Rice (*J. Amer. Chem. Soc.*, 1924, **46**, 2319—2326).—In view of the difference between the isomeric esters of benzoylacrylic acid (A., 1923, i, 218) and of *p*-methoxybenzoylacrylic acid (this vol., i, 287), the isomeric methyl and ethyl esters of *p*-ethoxybenzoylacrylic acid have been investigated. The stable yellow esters, like those of *p*-methoxybenzoylacrylic acid, are isomerised on exposure to sunlight in benzene solution, and the reverse change is effected in benzene solution containing a crystal of iodine. The methyl ester of the ethoxy compound, unlike that of the methoxy compound, is not polymerised on exposure to sunlight in the solid state, isomerisation alone taking place, and since the methoxy ester has the higher m. p., the physical state of the substance does not appear to be the sole determinant of polymerisation or isomerisation. *p*-Ethoxybenzoylacrylic acid itself does not polymerise on exposure to light. Both yellow and colourless esters are partly hydrolysed by dilute sodium carbonate and cold concentrated hydrochloric acid, yielding *p*-ethoxybenzoylacrylic acid, boiling dilute hydrochloric acid yielding also α-hydroxy-β-*p*-ethoxybenzoylpropionic acid. The colourless esters are first transformed into the yellow esters by hydrochloric acid. With semicarbazide, the esters of the *p*-ethoxy-acid behave like those of the *p*-methoxy-acid. The colourless esters yield an additive compound and its semicarbazone; the yellow esters yield, in addition, two isomeric semicarbazones. This reaction establishes the isomerism of the colourless ethyl ester, which could only be obtained liquid. *p*-Ethoxybenzoylacrylic acid itself yields a semicarbazone.

Methyl p-*ethoxybenzoylpropionate*, m. p. 53°, is converted by Kohler and Engelbrecht's method (A., 1919, i, 330) into *methyl* p-*ethoxybenzoylacrylate*, yellow needles, m. p. 81·5°; the colourless *isomeride*, m. p. 53°, can be obtained by direct esterification of p-*ethoxybenzoylacrylic acid*, yellow needles, m. p. 141—142° (*semicarbazone*, $C_{13}H_{15}O_4N_3$, m. p. 212° [decomp.]), obtained in 62% yield from maleic anhydride and phenetole by the Friedel–Crafts

reaction. *Ethyl* p-*ethoxybenzoylpropionate*, m. p. 51°, similarly yields *ethyl* p-*ethoxybenzoylacrylate*, yellow needles, m. p. 54°; colourless *isomeride*, an oil. On bromination in chloroform, methyl *p*-ethoxybenzoylacrylate yields a *dibromo* compound, $C_{13}H_{14}O_4Br_2$, m. p. 92°, the ethyl ester similarly yielding the *dibromo* derivative, $C_{14}H_{16}O_4Br_2$, m. p. 81°. Bromination of *p*-ethoxybenzoylacrylic acid in acetic acid yields αβ-*dibromo*-β-p-*ethoxybenzoylpropionic acid*, m. p. 151°. Hydrolysis of the esters of *p*-ethoxybenzoylacrylic acid with hydrochloric acid yields α-*hydroxy*-β-p-*ethoxybenzoylpropionic acid*, m. p. 132°. Colourless methyl *p*-ethoxybenzoylacrylate with 2 mols. of semicarbazide hydrochloride in methyl alcohol in the presence of sodium acetate yields *methyl* α-*semicarbazido*-β-p-*ethoxybenzoylpropionate*, m. p. 169°, together with the *semicarbazone* of the semicarbazide, m. p. 176° (decomp.). The yellow ester, on similar treatment, yields in addition to these two substances, the two isomeric *methyl* p-*ethoxybenzoylacrylate semicarbazones*, yellow, m. p. 173°, colourless, m. p. 149°. Similarly, colourless ethyl *p*-ethoxybenzoylacrylate yields *ethyl* α-*semicarbazido*-β-p-*ethoxybenzoylpropionate*, m. p. 154°, and its *semicarbazone*, m. p. 183° (decomp.), whilst the yellow isomeride yields in addition the two isomeric *ethyl* p-*ethoxybenzoylacrylate semicarbazones*, plates, m. p. 155°, and yellow needles, m. p. 140°.

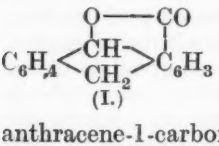
R. B.

Terephthalic Acid Derivatives. M. T. Bogert and P. S. Nisson (*Proc. Nat. Acad. Sci.*, 1924, **10**, 426—433; cf. A., 1920, i, 65).—*p*-Dihydroxy*iso*propylbenzene (*loc. cit.*) shows little or no physiological activity and has none of the properties of a local anæsthetic. Methyl terephthalate and magnesium ethyl iodide yield, not the expected pinacone, but p-*di*(α-*ethylpropenyl*)*benzene*, b. p. 149—151°/20 mm., in 46% yield. When magnesium *n*-butyl bromide is used, a gum, containing some unsaturated hydrocarbon, is obtained. Magnesium aryl halides, but not the alkyl derivatives, interact with terephthaloyl chloride to produce compounds of the type $COR{\cdot}C_6H_4{\cdot}COR$; thus, magnesium phenyl bromide affords *p*-dibenzoylbenzene. Methyl aminoterephthalate (cf. Kaufmann and Weissel, A., 1912, i, 863) interacts with ethyl iodide at 100° to give *methyl ethylaminoterephthalate*, m. p. 83·5°, and with ethyl sulphate at 150° to give *methyl diethylaminoterephthalate*, b. p. 191—192°/20 mm. When methyl aminoterephthalate is treated with magnesium methyl or ethyl bromide, or magnesium *n*-butyl bromide, only gummy products are obtained. Methyl dimethylaminoterephthalate (Kaufmann and Weissel, *loc. cit.*) and magnesium methyl iodide afford no pinacone, but 2 : 5-*di*iso*propenyldimethylaniline*, m. p. 62—63°; 2 : 5-*di*iso*propenyldiethylaniline* (?), b. p. 195—197°/18 mm., was similarly obtained. Methyl aminoterephthalate yields, however, with magnesium phenyl bromide, a glycol (pinacone), viz., 2 : 5-*di*(*hydroxydiphenylmethyl*)*aniline*, m. p. 202°; the dimethylamino and diethylamino esters similarly afforded 2 : 5-*di*(*hydroxydiphenylmethyl*)*dimethylaniline*, m. p. 185°, and 2 : 5-*di*(*hydroxydiphenylmethyl*)*diethylaniline*, m. p. 179°, re-

spectively. These compounds are sparingly soluble and valueless pharmacologically. W. A. S.

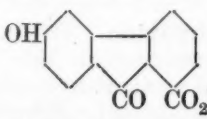
Synthesis of 3 : 5-Dihydroxycinnamic Acid. Y. ASAHINA and T. MATSUZAKI (*J. Pharm. Soc. Japan*, 1924, No. 509, 527—539).—3 : 5-Dihydroxybenzoic acid is prepared by heating a mixture of 100 g. of benzoic acid, 100 g. of phosphoric oxide, and 300 g. of fuming sulphuric acid (50% SO_3) at 280—300° for 10 hours, followed by fusion with potassium hydroxide (cf. Barth and Senhofer, *Annalen*, 1871, **159**, 217). The acid is changed into 3 : 5-dimethoxybenzaldehyde, through $(OMe)_2C_6H_3\cdot CO\cdot NHPh$, $(OMe)_2C_6H_3\cdot CCl{:}NPh$, and $(OMe)_2C_6H_3\cdot CH{:}NPh$. By applying Perkin's reaction to the aldehyde, 3 : 5-dimethoxycinnamic acid, m. p. 174°, is produced. On heating with hydrogen iodide, bromide, or other reagents, it gives no dihydroxy compound. When $(OMe)_2C_6H_3\cdot CCl{:}NPh$ is treated with zinc chloride, hydrogen chloride, and ether, a *chloro*-3 : 5-*dimethoxybenzaldehyde*, m. p. 129°, is obtained; *oxime*, m. p. 125°. When Perkin's reaction is applied to crude 3 : 5-diacetoxybenzaldehyde and the resulting acid is hydrolysed with sodium carbonate, 3 : 5-dihydroxycinnamic acid, $C_9H_8O_4,0{\cdot}5H_2O$, m. p. 244—245° (decomp.), is formed. It gives the above dimethyl derivative, m. p. 174°, by treatment with methyl sulphate. K. K.

Anthraquinonecarboxylic Acids. E. DE B. BARNETT, J. W. COOK, and H. H. GRAINGER (*Ber.*, 1924, **57**, [*B*], 1775—1781).—Anthraquinone-1-carboxylic acid is reduced by zinc and fuming hydrochloric acid in the presence of glacial acetic acid to a mixture of 10-anthrone-1-carboxylic acid, $C_6H_4\langle{}^{CO}_{CH_2}\rangle C_6H_3\cdot CO_2H$, m. p. 252°, and the *lactone* of 9 : 10-dihydro-9-anthranol-1-carboxylic acid (I), m. p. 277—278° after darkening at 264°; the latter compound is converted by boiling alcoholic potassium hydroxide solution into anthracene-1-carboxylic acid. The action of nitric acid (*d* 1·5) and glacial acetic acid on anthracene-1-carboxylic acid yields primarily the *acetate* of a nitrodihydroanthranol-1-carboxylic acid, m. p. 172° (decomp.), which is converted by pyridine into 9(?10)-*nitroanthracene*-1-*carboxylic acid*, decomp. 249°. Anthracene-1-carboxylic acid is readily brominated in boiling glacial acetic acid to 9(?10)-*bromoanthracene*-1-*carboxylic acid*, m. p. 281—282° (decomp.), but bromination does not proceed beyond this stage when excess of halogen is used. The action of bromine on anthracene-1-carboxylic acid in the presence of pyridine yields *anthracyl*-10-*pyridinium bromide*-1-*carboxylate*, $C_6H_3\langle{}^{CH\text{———}}_{C(NC_5H_5Br)}\rangle C_6H_3\cdot CO_2H,1{\cdot}5H_2O$. *Phenyl anthracene*-1-*carboxylate*, m. p. 207—209°, is converted by bromine (2 g.-mol.) into the ester of the monobromo-acid, but by a large excess of bromine into a mixture of the esters of the mono- and dibromo-acids. Anthracene-2-carboxylic acid, conveniently obtained


(I.)

by the reduction of 9-anthrone-2-carboxylic acid with zinc dust and ammonia, resembles the isomeric acid in its behaviour during nitration, yielding initially an additive product which is transformed by pyridine into a mixture of isomeric nitroanthracene-carboxylic acids which has not been separated into its components. On the other hand, it is transformed by bromine into a *dibromo-anthracene-2-carboxylic acid*, m. p. 335° (decomp.). 9-Anthrone-2-carboxylic acid is converted by acetic anhydride and pyridine into its *acetyl* derivative, m. p. 253—255° (decomp.), which is transformed by nitration and subsequent acetylation of the product into 10-*nitro*-9-*acetoxyanthracene*-2-*carboxylic acid*, m. p. 228° (decomp.), after previous softening. H. W.

2 : 4-Dihydroxybenzoyl-*o*-benzoic Acid and some of its Derivatives. W. R. Orndorff and E. Kline [with C. V. Shapiro] (*J. Amer. Chem. Soc.*, 1924, **46**, 2276—2291).—2 : 4-Dihydroxybenzoyl-*o*-benzoic acid, m. p. 208—209° (decomp.), is obtained in 68% yield by heating phthalic anhydride with resorcinol at 126°, the use of boric acid (Fischer and Bollmann, A., 1922, i, 936) being unnecessary. The acid is also obtained (in 89·5% yield) by decomposition of fluorescein with sodium hydroxide, whilst on heating above its melting point the acid is converted into fluorescein, phthalic anhydride, and water. The γ-fluorescein described by Liebig (A., 1912, i, 376) was not obtained, but the reactions prove that the formation of fluorescein takes place in two stages, the intermediate product being 2 : 4-dihydroxybenzoyl-*o*-benzoic acid, which is colourless when pure, and melts to a red liquid. Contrary to Baeyer's statement, well-crystallised *ammonium, sodium, potassium, silver, barium, calcium, zinc* (m. p. 80—90°), and *lead* salts have been prepared, to which the ketonic structure, $(OH)_2C_6H_3{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2M$, is assigned, the lactone structure, $(OH)_2C_6H_3{\cdot}C(OH){\cdot}C_6H_4$ (O——CO), being attributed to the free acid (cf. Orndorff and Kelley, A., 1922, i, 833). On heating with acetic anhydride and sodium acetate, the acid is converted into a colourless *triacetate*, $C_{14}H_7O_5Ac_3$, m. p. 134—135°, and not a diacetate as stated by Liebig (*loc. cit.*), which is readily hydrolysed by alcoholic sodium hydroxide, yielding the dihydroxy-acid and a small quantity of a reddish-brown substance probably identical with the orange *anhydride*, $C_{14}H_8O_4$, m. p. above 350°, obtained by the action of thionyl chloride on either the crude yellow or the pure dihydroxy-acid. The orange anhydride gives a deep red solution in sodium hydroxide which does not yield the dihydroxy-acid on boiling. The anhydride appears to give an acetate with acetic anhydride. The annexed formula is suggested for this anhydride. By treatment with excess of acetic anhydride the dihydroxy-acid yields the *anhydride* of the monoacetate described by Fischer and Bollmann (*loc. cit.*), $C_{14}H_7O_4Ac$, m. p. 135—136° (from glacial acetic acid), which when crystallised from dilute acetic acid yields Fischer and Bollmann's



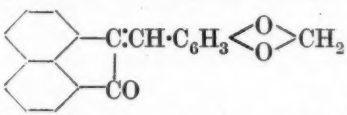
monoacetate, m. p. 161—162°. Dilute ethyl and methyl alcohol similarly convert the anhydride into the *ethyl* ester, m. p. 62—66°, and *methyl* ester, m. p. 110°, respectively. This anhydride has the structure $OAc\cdot C_6H_3<\begin{matrix}O-CO\\ |\\ CO\cdot C_6H_4\end{matrix}$. The monoacetate itself could not be obtained by acetylation with acetic anhydride, whilst with acetyl chloride the crude yellow dihydroxy-acid yields the *diacetate* of 2 : 4-dihydroxybenzoyl-*o*-benzoic anhydride, m. p. above 350°, together with a small quantity of an isomeric substance, $(C_{14}H_8O_2)_2Ac_2O$, which does not melt below 300°. The diacetate dissolves in sodium hydroxide, giving a deep purple solution, from which, on boiling, the orange anhydride, $C_{14}H_8O_4$, described above, together with a little dihydroxy-acid, is precipitated, and not the anhydride, $(C_{14}H_9O_4)_2O$, as stated by Graebe. The pure dihydroxy-acid on similar treatment yields a colourless *substance*, $(C_{14}H_7O_4Ac)_2$, m. p. 291—293° (decomp.), practically insoluble in sodium hydroxide and yielding on boiling the dihydroxy-acid with only a small amount of the orange anhydride. Esterification of the dihydroxy-acid in the presence of sulphuric acid yields the *ethyl* ester, m. p. 133—134° (cf. Tambor, A., 1910, i, 558), and *methyl* ester, m. p. 191—192°. 2 : 4-Dihydroxybenzoyl-*o*-benzoic acid yields a *phenylhydrazone*, $C_{20}H_{14}O_3N_2$ (+EtOH, lost at 130°), m. p. 260—261°, whilst on bromination in glacial acetic acid 3 : 5-dibromo-2 : 4-dihydroxybenzoyl-*o*-benzoic acid, m. p. 224° (decomp.; cf. Heller, A., 1895, i, 235; Meyer, A., 1897, i, 69), is obtained, which on heating above its m. p. is converted into eosin and phthalic anhydride, and on heating with resorcinol and zinc chloride at 160—180° yields *as*-dibromofluorescein. Dry ammonia converts the dibromo-acid into the unstable *triammonium* salt, $C_{14}H_8Br_2O_5+3{\cdot}5NH_3$, which loses 2 mols. of ammonia in a vacuum and the remaining 1·5 mols. in a current of air at 85°. The dibromo-acid forms a *triacetate*, $C_{14}H_5Br_2O_5Ac_3$, m. p. 179—182°, and the *anhydride* of a monoacetate, $C_{14}H_5Br_2O_4Ac$, m. p. 200—201° (decomp.). On heating with acetyl chloride, the dibromo-acid yields 3 : 5-*dibromo*-2 : 4-*diacetoxybenzoyl*-o-*benzoic anhydride*, m. p. 218°. R. B.

Bile Acids. XI. M. Schenck (*Z. physiol. Chem.*, 1924, **139**, 39—51).—The triketotricarboxylic acid, $C_{24}H_{32}O_9$, obtained by oxidation of *iso*bilianic acid (this vol., i, 179) is termed *bilisoidanic acid*; it reacts with hydroxylamine to form an amorphous monoxime. On reduction with zinc and acetic acid, dichloromonodeoxybilianic acid (Pregl, A., 1903, i, 318) gives a small yield of deoxybilianic acid; this establishes the position of the chlorine atoms in the former substance. E. S.

Compounds of Piperonal and Acetic Anhydride. W. P. Jorissen and P. A. A. Van der Beek (*Rec. trav. chim.*, 1924, **43**, 586—590).—The fusion curve of piperonal and acetic anhydride up to 60 mol.% of the latter shows no sign of a compound. When the compounds are heated together at 100° for 24 hours in presence of a trace of hydrobromic acid or phosphorus trichloride (cf.

Blanksma, A., 1910, i, 680) a fusion curve is obtained which shows that, besides a 1 : 1 molecular compound, there also exists a labile compound of 2 mols. of piperonal and 1 mol. of acetic anhydride. W. E. E.

Reaction of Aldehydes. III. R. De Fazi (*Gazzetta*, 1924, **54**, 658—667; cf. A., 1921, i, 568).—With piperonal, cuminaldehyde, *m*-tolualdehyde, cinnamaldehyde, *p*-dimethylaminobenzaldehyde, and furfuraldehyde, fluorene yields unsaturated condensation products which give various colorations with concentrated sulphuric acid, but on reduction form compounds giving no such coloration. Acenaphthene does not yield condensation products with these cyclic aldehydes under the conditions employed by the author, but acenaphthenone reacts with such aldehydes in presence of sodium hydroxide, the resulting compounds giving violet-red colorations with concentrated sulphuric acid. These compounds cannot, however, be formed when acenaphthene and cyclic aldehydes are placed in contact with sulphuric acid, since such conditions lead neither to the formation of acenaphthenone nor, if the latter is added, to the formation of either condensation products or coloration. The results obtained with indones (A., 1921, ii, 357) show that, with some organic compounds containing closed nuclei, the same coloration with sulphuric acid may be determined by the presence of the cyclostatic group $-CO\cdot CH{:}CH-$ as by $-CH_2\cdot CH{:}CH-$.



Piperonylideneacenaphthenone (annexed formula) forms canary-yellow needles, m. p. 159—160°; *4-hydroxy-3-methoxybenzylideneacenaphthenone*, $C_{20}H_{14}O_3$, from acenaphthenone and vanillin, m. p. 149—150°; p-*methoxybenzylideneacenaphthenone*, $C_{20}H_{14}O_2$, from anisaldehyde, canary-yellow needles, m. p. 97—98°; *cinnamylideneacenaphthenone*, $C_{21}H_{14}O$, yellow needles, m. p. 167—168°; p-*dimethylaminobenzylideneacenaphthenone*, garnet-red, stellar aggregates of needles, m. p. 158—160°, and *furfurylideneacenaphthenone*, $C_{17}H_{10}O_2$, golden-yellow prisms, m. p. 142—143°. T. H. P.

The Systems, Aldehydes–Organic Acids and Ketones–Organic Acids. M. Passerini (*Gazzetta*, 1924, **54**, 672—682).—The suggestion that, in the reaction of a carbylamine with an aldehyde or ketone in presence of an organic acid, the aldehyde or ketone first forms with the organic acid a labile additive compound (cf. A., 1922, i, 731) is verified by: (1) the electrical conductivities of mixtures of acetone with acetic acid, a minimum value being shown by the mixture containing the components in about molecular proportions; (2) the results of thermal analysis of the three systems formed by benzoic acid with *m*-nitrobenzaldehyde, piperonal, and benzil, respectively. These conclusions are in accord with those of Kendall and Brakeley (A., 1922, ii, 126). T. H. P.

Carbylamines. XI. Reaction of Phenylcarbylamine with Anil Derivatives of Aromatic *o*-Hydroxyaldehydes. M. Passerini (*Gazzetta*, 1924, **54**, 667—671).—In the formation of dianil

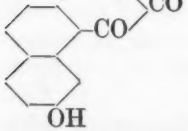
derivatives by the interaction of aromatic hydroxy compounds with carbylamines (cf. this vol., i, 57, 751 and succeeding abstract), either the carbylamine may act in its dimeric form, $(NR{:}C)_2$, or there may be two distinct stages, the anil derivative of the hydroxyaldehyde being formed first. The former of these interpretations is excluded by the observation that benzeneazophenylcarbylamine, which reacts in the same way as phenylcarbylamine with β-naphthol, has the simple molecular weight in freezing benzene. That the second explanation is the true one is shown by the formation of the dianil derivative of 2-hydroxy-1-naphthylglyoxal from phenylcarbylamine and the anil derivative of 2-hydroxy-1-naphthaldehyde, and by that of the dianil derivative of *o*-hydroxyphenylglyoxal from salicylideneaniline and phenylcarbylamine; benzylideneaniline does not, however, react with phenylcarbylamine under the conditions used.

The reaction between phenylcarbylamine and naphthols or phenol is evidently determined by the presence of the hydroxyl group, which imparts special properties to the methinic group in the ortho position; the same influence is probably exerted by the hydroxyl group of the anil derivatives of the hydroxyaldehydes.

T. H. P.

Carbylamines. X. Reaction of Aromatic Carbylamines with Naphthols and with Phenols. M. Passerini (*Gazzetta*, 1924, **54**, 633—640).—The action of phenylcarbylamine on various hydroxy derivatives of benzene and naphthalene has been investigated (cf. this vol., i, 57, 751). With 2 : 7-dihydroxynaphthalene, the reaction is similar to that occurring with β-naphthol, 2 mols. of the carbylamine and 1 mol. of the hydroxy compound interacting; no tetra-anil is obtained. Phenol, thymol, and resorcinol also react with phenylcarbylamine, but the products formed are syrupy, and only in the first case could a small amount of the dianil be separated. The reaction proceeds well with β-naphthol and benzeneazophenylcarbylamine.

The *dianil* derivative of 2 : 7-*dihydroxy*-1-*naphthylglyoxal*, $C_{10}H_5(OH)_2{\cdot}C(:NPh){\cdot}CH:NPh$, obtained from 2 : 7-dihydroxynaphthalene and phenylcarbylamine, forms pale yellow needles, m. p. 174—176°, and its *dibenzoyl* derivative, $C_{38}H_{26}O_4N_2$, orange-red crystals, m. p. 154—156° (decomp.). Phenylhydrazine converts the dianil into 2 : 7-*dihydroxy*-1-*naphthylglyoxal diphenylhydrazone*, $C_{10}H_5(OH)_2{\cdot}C(:N{\cdot}NHPh){\cdot}CH:N{\cdot}NHPh$, m. p. 220° (decomp.), and, when boiled with potassium hydroxide solution, the anil yields the *lactone* of 2 : 7-*dihydroxy*-1-*naphthylglyoxylic acid* (annexed formula), which has a distinctly acid reaction and forms lustrous, yellow crystals, decomp. 280—282°; 2 : 7-*dihydroxynaphthalene*-1-*carboxylic acid*, obtained by oxidising this lactone with hydrogen peroxide in acetic acid solution, has m. p. 275°.



The *dibenzeneazoanil* derivative of 2-*hydroxy*-1-*naphthylglyoxal*, $OH{\cdot}C_{10}H_6{\cdot}C(:N{\cdot}C_6H_4{\cdot}N:NPh){\cdot}CH:N{\cdot}C_6H_4{\cdot}N_2Ph$, forms minute, dark-

red crystals, m. p. 263°, and is converted by phenylhydrazine into 2-hydroxy-1-naphthylglyoxal diphenylhydrazone (cf. this vol., i, 57).

The *dianil* derivative of o-*hydroxyphenylglyoxal*,

$$OH\cdot C_6H_4\cdot C(:NPh)\cdot CH:NPh,$$

obtained from phenol and phenylcarbylamine, yellow needles, m. p. 150—152°, yields *o*-hydroxyphenylglyoxal diphenylhydrazone when treated with phenylhydrazine. T. H. P.

Catalytic Reduction of Oximes in the Presence of Colloidal Palladium. W. Gulewitsch.—(See i, 1285.)

Magnesium Acetylenyl Bromide. J. Salkind and A. Rosenfeld.—(See i, 1291.)

Electrolytic Reduction of Piperitone. A. R. Penfold and F. R. Morrison (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 215—217).—An almost quantitative yield of *iso*menthone is obtained by the electrolytic reduction of piperitone. [Cf. *B.*, 1924, 926.] W. T. K. B.

Phenacyl Mercaptan and Related Substances. B. Groth (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 1, 1—63).—The preparation of phenacylmercaptan by several methods is described; a number of its derivatives and certain phenacylthiocarbonates were also prepared.

The interaction of phenacyl bromide and sodium hydrogen sulphide solution at 15° gives only 13% of the theoretical yield of phenacyl mercaptan, together with diphenacyl sulphide. Phenacyl bromide with Bender's salt in aqueous alcohol at 0° gives S-*phenacyl* O-*ethyl thiocarbonate*, $C_{11}H_{12}O_3S$, b. p. 152°/1·6 mm., 175—176°/3 mm., d_4^{15} 1·1948, n_D^{15} 1·554; *semicarbazone*, m. p. 142—143°; with potassium xanthate it gives S-*phenacyl* O-*ethyl dithiocarbonate*, m. p. 32° (*phenylhydrazone*, m. p. 64°); with potassium trithiocarbonate it gives *phenacyl trithiocarbonate*, $(COPh\cdot CH_2\cdot S)_2CS$ (yield 90%), obtained in two forms, m. p. 103—104° and m. p. 110°; *bisphenylhydrazone*, m. p. 139—140°, after keeping, m. p. 146—147°. Alkaline hydrolysis of these thiocarbonates, under varying conditions, gave no phenacyl mercaptan, showing the sulphur atom to be loosely attached to the phenacyl group. Boiling 20% nitric acid with the third ester gave benzoic acid and at 60—70° gave SS-*diphenacyl dithiocarbonate*, m. p. 98°; *bisphenylhydrazone*, m. p. 162° (decomp.).

Phenacyl bromide reacts with potassium carbothiolonglycollate solution at 0°, forming phenacyl trithiocarbonate and *phenacylcarbothiolonglycollic acid*, $COPh\cdot CH_2\cdot S\cdot CS\cdot O\cdot CH_2\cdot CO_2H$, m. p. 107°, which is precipitated by acidification of the filtrate; it forms acid *sodium* and *potassium* salts; *calcium* ($+4H_2O$), *strontium* ($+5H_2O$), *barium* ($+2H_2O$), *cupric*, *lead*, *magnesium*, and *zinc* salts; *methyl* ester, m. p. 76°; *ethyl* ester, m. p. 51°; *phenylhydrazone*, m. p. 119—120°. Hydrolysis with acetic acid gave a good yield of phenacyl mercaptan. Hydrolysis with sodium carbonate gave diphenacyl disulphide, and acetophenone or phenacyl trithiocarbonate according to the conditions; alcoholic potassium hydroxide gave potassium

carbothiolonglycollate (cf. Ahlqvist, A., 1919, i, 435). Oxidation of phenacylcarbothiolonglycollic acid with neutral permanganate gives *phenacylcarbothiolglycollic acid*, $COPh\cdot CH_2\cdot S\cdot CO_2\cdot O\cdot CH_2\cdot CO_2H$, m. p. 77° (yield 80%); acid *sodium* salt; *barium* salt ($+3H_2O$); *phenylhydrazone*, m. p. 136—137°. By the action of water or weak acid, this also gave phenacyl mercaptan, yield 68%.

Potassium dithiocarbaminoacetate (cf. Körner, A., 1908, i, 509) with phenacyl bromide forms *phenacyldithiocarbaminoacetic acid*, $COPh\cdot CH_2\cdot S\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 103° (yield 88%); *sodium* salt ($+2H_2O$ and $+7H_2O$). With alkali, it gives a 54% yield of phenacyl mercaptan. By (*a*) heating at 119°, (*b*) steam distillation, or, best, (*c*) action of acetic acid on the sodium salt solution at 95—100°, water is eliminated, forming *2-thion-4-phenylthiazoline-3-acetic acid*, $PhC{:}CH\cdot S\cdot CS\cdot N\cdot CH_2\cdot CO_2H$; *sodium* salt ($+3\frac{1}{2}H_2O$); *barium* salt ($+2H_2O$ and $+7H_2O$); *methyl* ester, m. p. 115—116°; *ethyl* ester, m. p. 72—73°.

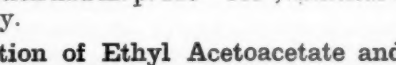
By decomposition of sodium phenacylcarbothiolonglycollate with acetic acid at 80—95°, *phenacyl mercaptan*, $COPh\cdot CH_2\cdot SH$, m. p. 23—24°, b. p. 103°/1·5 mm., 116—118°/4 mm., 140—142°/16—18 mm., n_D^{25} 1·594, d_4^{25} 1·1713, is obtained in 70% yield; *semicarbazone*, m. p. 164—165°; *phenylhydrazone*, m. p. 90—91°; *oxime*, m. p. 70°. It behaves as a pseudo-acid and its *sodium* salt may have the structure $S\cdot CH_2\cdot CPh\cdot ONa$, but only one benzoyl derivative could be obtained. *Phenacyl thiobenzoate*, m. p. 84—85°, was also synthesised from potassium thiobenzoate and phenacyl bromide; *phenylhydrazone*, m. p. 108°. Reduction of the mercaptan by Clemmensen's method gives ethylbenzene. With alcoholic lead acetate, it gives *lead phenacyl sulphide* (gradual decomp.). With phenacyl bromide and sodium ethoxide, *diphenacyl sulphide*, m. p. 77°, is formed. The mercaptan has a simple molecule and does not polymerise, alone or with zinc; condensation products are formed by the action of calcium chloride. Alcoholic hydrochloric acid converts it into 2 : 5-*diphenyl*-1 : 4-*dithiine*, m. p. 118°. This, or phenacyl mercaptan with ethyl mercaptan in presence of hydrochloric acid, gives a condensation product, m. p. 161°, either 2 : 5-*diethylmercapto*-2 : 5-*diphenyl*-1 : 4-*dithiane* or 3 : 6-*diethylmercapto*-2 : 5-*diphenyl*-1 : 4-*dithiane*. Similarly, phenacyl and benzyl mercaptans interact, forming a *compound*, $C_{30}H_{28}S_4$, m. p. 216—217° (on rapid heating) or 206—207° (slow heating). The properties of phenacyl mercaptan are compared with those of hydroxyketones.

In the above experiments, the yield of mercaptan was ascertained by oxidising its solution with iodine in the presence of potassium iodide to *diphenacyl disulphide*, m. p. 81° (yield 90%); *bisphenylhydrazone*, m. p. 150°. When potassium acts on alcoholic diphenacyl disulphide, ether precipitates the *dipotassium* salt, from which acid liberates a *dienol* form, m. p. 168—170° (or 135° on rapid heating); the *dibenzoyl* derivative, m. p. 168°, is hydrolysed to benzoic acid and is regarded as bis-β-hydroxystyryl αα′-disulphide. The action of potassium on alcoholic diphenacyl disulphide gives, after 2 weeks,

diphenacyl, m. p. 144—145°. The disulphide is more unstable than the mercaptan, sulphur being readily removed by the action of alkali, whilst silver nitrate precipitates silver sulphide. F. M. H.

Isomerism of the Styryl Alkyl Ketones. I. Isomerism of 2-Hydroxystyryl Methyl Ketone. A. McGookin and I. M. Heilbron (*J. Chem. Soc.*, 1924, **125**, 2099—2105).—The yellow 2-hydroxystyryl methyl ketone prepared according to Harries (A., 1892, 169) does not condense with gentisaldehyde, but is converted into the colourless isomeride, m. p. 139°, described by Tiemann and Kees (A., 1885, 1074). Protocatechualdehyde, *p*-hydroxybenzaldehyde, or vanillin also brings about the conversion. Vanillin gives a nearly theoretical yield of pure substance. Exposure of an alcoholic solution of the yellow form to the light of a quartz mercury lamp causes complete isomerisation. The colourless isomeride condenses with salicylaldehyde to form 2 : 2′-dihydroxydistyryl ketone, yellow needles, m. p. 159°; Decker and Felser (A., 1908, i, 906) found m. p. 168°. On methylation, 2-methoxystyryl methyl ketone is formed, m. p. 50°, identical with that prepared from the yellow isomeride. The sodium salt was obtained in golden-coloured crystals. An attempt to prepare the sodium salt of the yellow isomeride by treatment of the ketone with alcoholic sodium ethoxide and fractional precipitation of the crimson reaction liquid with chloroform resulted in the separation of (i) lustrous bottle-green crystals of the sodium salt of 2 : 2′-dihydroxydistyryl ketone, (ii) an orange salt, (iii) golden-yellow crystals, and (iv) a pale yellow salt, the sodium derivative of salicylaldehyde. The orange salt is probably the sodium salt of the yellow isomeride, although on dissolving in water and acidifying the solution only the colourless isomeride was obtained. The oxime, semicarbazone, and phenylhydrazone of the colourless ketone are identical with those obtained from the yellow isomeride. The isomerism is considered to be of the *cis-trans* type, the yellow isomeride being the *cis*-form. It is the more labile and tends to disrupt in presence of alkali. In all cases where isomeric styryl ketones have been obtained the isomerides have identical m. p., and one form appears to pass into the other at or just below the m. p. The colourless isomerides of 5-bromo-2-hydroxystyryl methyl ketone and 3-methoxy-4-hydroxystyryl methyl ketone were prepared from the yellow forms by methods similar to the above. The yellow form of 4 : 5-methylenedioxystyryl methyl ketone, m. p. 107° (Haber, A., 1891, 704), on purification had m. p. 110—111°, identical with that of the colourless variety. A. C.

Interaction of Ethyl Acetoacetate and *o*-Hydroxydistyryl Ketones. I. M. Heilbron and T. A. Forster (*J. Chem. Soc.*, 1924, **125**, 2064—2068; cf. this vol., i, 413).—3-o-*Hydroxyphenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexen*-1-*one*,



(I.),

m. p. 240° (with 1 mol. of methyl alcohol), was prepared by condensing 2 : 2′-dihydroxydistyryl ketone with ethyl acetoacetate in

aqueous sodium hydroxide solution. It was accompanied by 4-*o*-hydroxystyracyldihydrocoumarin,

$$HO\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot CH_2\cdot \underset{C_6H_4\text{--}O}{\overset{}{CH}}\cdot CH_2\!>\!CO,$$

m. p. 235°, *methyl ether*, m. p. 130°. The hexenone gives a deep red, the coumarin only a pale yellow coloration with concentrated sulphuric acid. 3-o-*Methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 128°, was obtained on methylating the corresponding dihydroxycyclohexenone. 2 : 2′-*Dimethoxydistyryl ketone*, m. p. 127°, condenses with sodium ethyl acetoacetate in boiling alcohol forming *ethyl* 3-o-*methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 159°. The carbethoxy group could not be removed by either acid or alkali. 3-o-*Hydroxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 172°, was similarly prepared from 2′-methoxy-2-hydroxydistyryl ketone. Its methyl ether is identical with the dimethyl ether of I. *Ethyl* 3-o-*methoxyphenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 159—161°, was obtained from the alkaline filtrate of the above hexenone. 2-*Acetyl*-3-o-*methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 174°, was prepared by condensing 2 : 2′-dimethoxydistyryl ketone with acetylacetone. On heating it with a mixture of potassium methoxide and hypoiodite, the acetyl group was split off and a methyl ether obtained identical with that from I. A. C.

Chalkones and Hydrochalkones. V. Tognazzi (*Gazzetta*, 1924, **54**, 697—704; cf. Bargellini, A., 1912, i, 118; 1913, i, 59, 90; 1914, i, 1074; 1915, i, 19).—When reduced by means of hydrogen in presence of platinum or palladium black, chalkones usually undergo hydrogenation at the double linking, but not at the carbonyl group, the only two known exceptions to this rule being 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone, which yields 2 : 4 : 6 : 3′ : 4′-pentamethoxy-$\alpha\gamma$-diphenylpropane, and 4 : 6-dimethoxy-2-ethoxyphenyl 3 : 4-dimethoxystyryl ketone, which also yields the corresponding propane derivative (cf. Freudenberg, A., 1920, i, 752). Of a number of other chalkones examined by the author, only one, namely, furfurylidene-2 : 4 : 5-trimethoxyacetophenone, appears to absorb more than 2 atoms of hydrogen per molecule, but the product of the reaction was resinous and could not be purified. Certain compounds analogous to the chalkones, such as distyryl ketone, also seem to absorb, in presence of platinum black, more hydrogen than is required by the double linkings.

p-*Methoxyphenyl* p-*methoxystyryl ketone* (4 : 4′-*dimethoxychalkone*), prepared from anisaldehyde and *p*-methoxyacetophenone, has m. p. 100—102°, and p-*methoxyphenyl* β-p-*methoxyphenylethyl ketone* has m. p. 29—31°.

4′-*Methoxy*-3 : 4-*dioxymethylenechalkone* [p-*anisyl piperonylidenemethyl ketone*], from *p*-methoxyacetophenone and piperonaldehyde (cf. Scholtz and Meyer, A., 1910, i, 562), gives p-*anisyl piperionylethyl ketone*, $C_{17}H_{16}O_4$, m. p. 56—58°, on reduction in presence of platinum black.

p-*Anisyl furfurylidenemethyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$, from *p*-methoxyacetophenone and furfuraldehyde, m. p. 79—81°, yields an oily reduction product. 2 : 4 : 5-*Trimethoxyphenyl furfurylidenemethyl ketone* has m. p. 116—118°.

2-Hydroxy-4-methoxyphenyl piperonylidenemethyl ketone (piperonalpaeonol; cf. Emilewicz and von Kostanecki, A., 1899, i, 368) gives *2-hydroxy-4-methoxyphenyl piperonylethyl ketone*, $C_{17}H_{16}O_5$, white needles, m. p. 85—87°, on reduction.

2′ : 4′ : 5′-Trimethoxy-3 : 4-dioxymethylenechalkone has m. p. 186—188° (cf. Bargellini and Avrutin, A., 1911, i, 68), and 2 : 4 : 5-*trimethoxyphenyl piperonylethyl ketone*, $C_{19}H_{20}O_6$, has m. p. 131—133°. T. H. P.

Functions of Chromophores. X. The Quinone Chromophore. II. J. Lifschitz [with J. Zimmermann, H. Lourié, and G. A. Ten Bokkel-Huinink] (*Rec. trav. chim.*, 1924, **43**, 403—419).—All groups which contain a cross-conjugated system of unsaturated linkings may be regarded as quinonoid chromophores. This structure, rather than its diketonic nature, determines the chromophoric character of the quinone in the narrow sense; the central carbon atom is the source of the colour. This conception permits of a single explanation of the optical properties of dyes and their relationship to the quinones (cf. this vol., i, 654). H. J. E.

Functions of Chromophores. XI. The Quinone Chromophore. III. J. Lifschitz (*Rec. trav. chim.*, 1924, **43**, 654—670).—The views previously developed (this vol., i, 654 and preceding abstract) on the subject of the *p*-quinone chromophore are successfully applied in the discussion of the molecular compounds of quinone, the halochromism of triphenylmethane derivatives and ketones and of free radicals. The views of earlier workers in these fields are critically discussed. W. E. E.

Colour of the Simple Quinoneimines and their Salts. II. Some New Quinoneimines and their Stability. B. Cordone (*Helv. Chim. Acta*, 1924, **7**, 956—964; cf. this vol., i, 214).—Quinoneimines are particularly prone to two reactions and, according to circumstances, one of the two is generally favoured to the exclusion of the other. Hydrolysis to the corresponding quinone in presence of water is slow at the ordinary temperature, but at the boiling point the action is rapid and quantitative. The more heavily the nucleus is substituted by alkyl groups, the more rapid is the hydrolysis. The tendency to polymerise is affected by light, temperature, and the presence of acids, but chiefly by the number of substituent alkyl groups. The presence of even a single alkyl group in the nucleus of a quinoneimine will greatly lessen its tendency to polymerise, particularly if it is adjacent to the imino group. The effect of acids varies. In ether solution, and more especially in the dry state, anhydrous acids cause polymerisation. The tendency of the quinoneimine bases to "quinonise" in the presence of water is changed by acid to a tendency to polymerise.

On the other hand, homologues of benzoquinoneimines containing in the nucleus at least two alkyl groups and hence possessing relatively little tendency to polymerise are caused to "quinonise" by mineral acids in aqueous solution. The hydrochlorides undergo this change more easily than the sulphates. The picrates of the quinoneimines polymerise like the free bases, but more slowly: picric acid has no hydrolysing effect, but retards condensation. *Thymoquinone-di-imine* is obtained in ethereal solution by oxidising *p*-diamino-cymene with silver oxide; the *monopicrate* exists in a yellow and a red form. In aqueous solution, the sulphate and the chloride readily form the quinone. The sulphate liberates iodine from potassium iodide. Toluquinone-2-imine, from *p*-amino-*m*-cresol, is easily isolated and may be preserved for a long time. The monopicrate (two forms) is more stable than the base. No other monosalt is obtainable, but the yellow solution of the di-salt in concentrated sulphuric acid is stable. The aqueous solution of the base is stable unless heated, when the quinone is formed. Toluquinone-3-imine, from *p*-amino-*o*-cresol, is too unstable to be isolated. All the mono-salts polymerise immediately except the picrate, which exists in a yellow, amorphous form and a dense, red, crystalline form. W. E. E.

Colour and Constitution. IX. F. KEHRMANN (*Helv. chim. Acta*, 1924, **7**, 964—968; cf. A., 1922, ii, 333).—In view of Piccard's observation (A., 1913, i, 895) that certain quinonedi-imines, particularly the oxidation product of *p*-dimethylaminodiphenylamine, give di-salts lighter in colour than their mono-salts, the rule previously formulated must be modified to this: "If the unsaturation persists after salt formation, the addition of acids to unsaturated groupings results most frequently in a deepening of colour, even if tervalent nitrogen becomes quinquevalent. This deepening occurs regularly if the chromophore is open to the attack of the acid only at one point. When two basic groups are present, the neutralisation of the first leads to a deepening, whilst that of the second may, exceptionally, cause a lightening of the colour."

The mono-salts of the quinonedi-imines under discussion are reddish-violet, the di-salts reddish-orange; Piccard's observations on the colour of these salts are incorrect. W. E. E.

Derivatives of Arylaminomercaptonaphthaquinones. FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING (D.R.-P. 386998; from *Chem. Zentr.*, 1924, i, 2634).—The derivatives are prepared by treating 3-chloro-2-arylamino-1 : 4-naphthaquinone derivatives with alkali sulphides. Thus, 3-*chloro*-2-*anilino*-1 : 4-*naphthaquinone* (from 2 : 3-dichloro-1 : 4-naphthaquinone and aniline) is boiled for a short time with sodium sulphide to give a blue solution of the *sodium* salt of 2-*anilino*-3-*mercapto*-1 : 4-*naphthaquinone*, from which hydrochloric acid precipitates the dark violet *mercaptan*, which is converted by atmospheric oxidation into *benzonaphtho-parathiazinequinone*. On heating 2 : 3-dichloro-1 : 4-naphthaquinone with aceto-*p*-phenylenediamine, 3-*chloro*-2-p-*acetamido*-

phenylamino-1 : 4-*naphthaquinone* is obtained as red crystals, m. p. 271°; this yields the corresponding *mercapto* compound, which is oxidised by the air to the corresponding green p-*thiazine*; this is further oxidised by hydrogen peroxide to the brownish-red *sulphoxide* of an *acetamidobenzonaphthoparathiazinequinone*.

F. A. M.

Photochemical Behaviour of Methylanthraquinones. A. Schaarschmidt and K. Kasai (*Ber.*, 1924, **57**, [*B*], 1671—1673).—Methylanthraquinones may be arranged in the following order of decreasing sensitiveness towards light: 4-chloro-1-methylanthraquinone, 2-methylanthraquinone, 3-bromo-2-methylanthraquinone, 1-nitro-2-methylanthraquinone, 1-methylanthraquinone, 3-chloro-2-methylanthraquinone, 1-chloro-2-methylanthraquinone, 1-chloro-2-dibromomethylanthraquinone, 1 : 3-dimethylanthraquinone. 1 : 3-Dimethylbenzophenone is not appreciably altered by exposure to light. Since 4-chloro-1-methylanthraquinone becomes similarly altered when illuminated in an atmosphere of nitrogen or in a high vacuum, the change is considered to consist in a transformation into a coloured quinonoid modification which is not completely converted into the original form when rapidly crystallised from alcohol. H. W.

Tetrahydroxydimethylanthraquinone. G. Flumiani (*Monatsh.*, 1924, **45**, 43—49).—Two compounds prepared by Brunner (*ibid.*, 1881, **2**, 466) are shown to be 1 : 4 : 5 : 8-tetrahydroxy-2 : 6-dimethylanthraquinone and 2 : 6-dimethylanthracene. Brunner's starting point is now recognised as 3 : 6-dihydroxy-*p*-toluic acid (Schmid, A., 1911, i, 780; Herrmann, A., 1877, ii, 319; Baeyer, A., 1886, 445). By treatment with concentrated sulphuric acid at 120—130°, it gives a heterogeneous solid which after many recrystallisations from ethyl benzoate yields 1 : 4 : 5 : 8-*tetrahydroxy*-2 : 6-*dimethylanthraquinone*, a red powder; when heated slowly it sinters at 200° and sublimes, with slight charring, from 260°; on rapid heating, m. p. 290—300° with sublimation. Benzoic anhydride at 130—135° converted it into a *dibenzoyl* derivative, white needles, m. p. 220°. Boiling acetic anhydride, with sodium acetate, formed the *tetra-acetyl* derivative, m. p. 235—236° (yield 50%). Distillation of the tetrahydroxy compound with zinc dust in a current of hydrogen gave 2 : 6-*dimethylanthracene* (yield 20%); m. p. 242—243°, after many recrystallisations. This is oxidised by chromic acid in acetic acid solution to 2 : 6-dimethylanthraquinone.

F. M. H.

Formulæ of Dicyclic Terpenes. C. Slawinski (*Bull. Soc. chim.*, 1924, [iv], **35**, 1195—1198).—The formulæ proposed for the dicyclic terpenes by Dupont (A., 1922, i, 1042) involve two new conceptions of oscillating bonds and the linking of three valencies of three separate carbon atoms with the " bridge " carbon atom, which introduce fresh complications. The author contends that his extended theory of conjugated bonds (cf. A., 1899, i, 529) is sufficient to explain the transformations of these terpenes. R. B.

Chemistry of Cadinene. I. G. G. HENDERSON and A. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 1992—1996).—Cadinene of greater purity than 70% could not be obtained by the repeated fractional distillation under reduced pressure of oil of cubebs. The fraction of b. p. 125—140°/12 mm. was mixed with glacial acetic acid (⅓ vol.) and cadinene precipitated as the hydrochloride. Pure cadinene was obtained from the latter by means of anhydrous sodium acetate. Agitation of a solution of cadinene hydrochloride in glacial acetic acid with silver acetate at 70° resulted in the formation of a light yellow oil, which was steam-distilled, and a saturated *compound*, $C_{15}H_{28}O_2$, m. p. 194—195°, probably a glycol, was isolated from the residue in 2% yield. The volatile portion consisted of cadinene and an unsaturated *compound*, $C_{15}H_{25}OH$, apparently the alcohol cadinol (cf. Semmler and Jonas, A., 1915, i, 63). It formed a *bromo-dibromide*, $C_{15}H_{25}OBr_3$, an unstable, oily liquid. These hydroxy compounds were not obtained when cadinene hydrochloride was treated with silver acetate in ethereal or alcoholic solution, the sole product being cadinene. Cadinene was not hydrated by heating its acetic acid solution with 30% sulphuric acid, but yielded a brown oil the greater part of which was volatile in steam and consisted of an isomeric unsaturated hydrocarbon, termed iso*cadinene*, b. p. 125—128°/12 mm., d_4^{20} 0·9160, n_D^{20} 1·5141. The same substance was obtained on heating cadinene with glacial acetic acid at 230—235° for 24 hours. It had $[\alpha]$ −1·0°, quickly resinified in air, absorbed bromine with evolution of hydrogen bromide, and formed no solid nitrosochloride, nitrosite, or nitrosate. A sesquiterpene was isolated from the liquid left after isolating cadinene hydrochloride from oil of cade which appears very similar to one described by Lepeschkin (A., 1908, i, 278). A. C.

Essential Oil of *Backhousia angustifolia*. I. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 300—312).—The oil, obtained in a yield of 1·08% by steam-distillation of the leaves and terminal branchlets, contains 75% of a hitherto undescribed *phenol* ($C_{10}H_{14}O_2$, b. p. 122—124°/10 mm.) of poor germicidal value, together with *d*-α-pinene, β-pinene, cineol, alcoholic compounds (*e.g.*, α-terpineol), a sesquiterpene, and a stearoptene ($C_{15}H_{16}O_5$; probably a lactone) of m. p. 118—119°. The phenol is an almost colourless, viscous liquid, giving a brilliant orange-red coloration with alcoholic ferric chloride. It forms a crystalline *ammonium* derivative, $C_{10}H_{17}O_3N$, m. p. 135—137°, and a purple, crystalline *copper* derivative, $(C_{10}H_{12}O_2)_2Cu$, m. p. 193—194°. Oxidation of the phenol with alkaline potassium permanganate gives potassium acetate and potassium carbonate. W. T. K. B.

Essential Oil of *Darwinia grandiflora* and the Presence of a New Acetic Ester. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 237—248).—Distillation of the leaves and terminal branchlets of *Darwinia grandiflora* yields a mobile, pale yellow oil (0·35%), the main constituents of which are *d*-α-pinene, an unidentified terpene (b. p. 175—177°), an acetic ester ($C_{10}H_{18}O$; b. p. 108—116°/10 mm.) named *darwinol acetate* and not

hitherto described, a sesquiterpene (b. p. 130—133°/10 mm.; possibly identical with eudesmene) and corresponding sesquiterpene alcohol (b. p. 134—138°/5 mm.), a stearoptene (m. p. 103—104°; probably a phenol ether), and small quantities of *iso*valeraldehyde, amyl alcohol, and an ester. W. T. K. B.

Essential Oils of *Callistemon lanceolatus* and *C. viminalis*. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 131—139).—The essential oil of *Callistemon lanceolatus*, obtained in a yield of 0·06—0·22%, contains cineol, dipentene, limonene, terpineol, sesquiterpene, and a small amount of phenols. *C. viminalis* appears to exist in two varieties, that from New South Wales yielding an oil (0·13—0·22%) containing *d*-α-pinene, cineol (about 30%), phenol (2%), sesquiterpene, and probably terpineol, whilst the oil from the Queensland variety (0·21—0·22%) contains cineol (60—80%), dipentene, limonene, terpineol, sesquiterpene, and phenol (about 0·5%). W. T. K. B.

Germicidal Values of Commercial Eucalyptus Oils and their Pure Constituents, with Observations on the Value of Concentrated Disinfectants. A. R. PENFOLD and R. GRANT (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 80—89).—The Rideal–Walker coefficients of a number of eucalyptus oils and their chemically pure constituents are tabulated. Terpenes (*e.g.*, pinene, phellandrene, limonene), sesquiterpenes, and sesquiterpene alcohols possess poor germicidal properties, whilst ketones (piperitone type), alcohols (piperitol and geraniol types), aromatic and open-chain aldehydes (cuminal, citral, and citronellal types), and phenols (*e.g.*, australol) possess well-marked germicidal properties. The effect of dilution on the coefficient of various germicidal preparations, including those with tar oils and phenol, is discussed, and it is shown that the germicidal value of a disinfectant is greater the greater the initial dispersion, provided dilution is made when the soap solution is added. W. T. K. B.

Germicidal Values of Australian Essential Oils (exclusive of Eucalypts) and their Pure Constituents, together with those of some Essential Oil Isolates and Synthetics. I. A. R. PENFOLD and R. GRANT (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 211—215; cf. preceding abstract).—The Rideal–Walker coefficients of the above are tabulated. Of the crude oils examined that from *Backhousia citriodora* has the highest coefficient (16; principal active constituent, citral) and that from *Homoranthus virgatus* the lowest (1; principal active constituent, *d*-α-pinene). Of the pure constituents thymol has the highest coefficient (25) and leptospermol the lowest (<1). W. T. K. B.

Constitution of Lichenol. A. S. PFAU (*Parfums de France*, 1924, No. 16, 137).—The compound, lichenol, m. p. 72—73°, found by Gattefossé (*Parfumerie moderne*, 1911, **4**, 6) to be the chief constituent of oak moss (*Evernia prunastri*, Ach.) oil, has m. p. 73·5—74° and is identical with ethyl evernate (Pfau, this vol., i, 512). CHEMICAL ABSTRACTS.

Isoprene and Caoutchouc. VII. Homologues of Hydrocaoutchouc. H. STAUDINGER and W. WIDMER (*Helv. Chim. Acta*, 1924, **7**, 842—848; cf. A., 1922, i, 1043).—The hydrohalides of caoutchouc are colloids which very readily lose hydrogen halide. To explain this, however, no special hypothesis is needed (cf. Pummerer and Burkhard, A., 1923, i, 49), the hydrohalides being regarded as hydrocaoutchouc, in which the tertiary hydrogen atom is substituted by halogen. Caoutchouc hydrobromide does not react with magnesium alkyl iodide, but with zinc dimethyl and zinc diethyl, methyl- and ethyl-hydrocaoutchouc, respectively, are easily obtained. Unless the reaction mixture is well cooled, the homologue is in both cases contaminated with a saturated isomeride of caoutchouc formed by ring closure after loss of methane (or ethane) and hydrogen halide. The new homologues of hydrocaoutchouc possess essentially the same physical and chemical properties as the parent. Above all, they are colloids. As paraffin hydrocarbons, they are stable towards permanganate, nitric acid, and bromine. They resemble hydrocaoutchouc in giving, on heating, fission products of olefinic character. The previous observation that saturated hydrocarbons may be colloids is confirmed. Together with its chemical properties, the colloidal nature of hydrocaoutchouc is direct evidence in favour of the new conception of the structure of caoutchouc (A., 1922, i, 1043). Harries (A., 1923, i, 693) has asserted that the action of high-pressure hydrogen on caoutchouc at 270° gives pyrogenic decomposition products. This cannot be true, however, because pyrogenic decomposition of caoutchouc gives molecular disperse decomposition products, which would yield, on reduction, molecular disperse reduction products. Harries' objection is further vitiated by the low-temperature transformation of caoutchouc into the colloidal homologues of hydrocaoutchouc. W. E. E.

Synthesis of Amygdalin. R. KUHN and H. SOBOTKA (*Ber.*, 1924, **57**, [*B*], 1767—1769).—Bromoacetogentiobiose is converted by ethyl *dl*-mandelate and silver oxide into a mixture of ethyl *d*-hepta-acetylamygdalate, m. p. 212·5—213·5° (corr.), $[\alpha]_D^{20}$ −72·8° in chloroform, and ethyl *l*-hepta-acetylamygdalate, m. p. 189·5—191° (corr.), which are separated from one another by fractional crystallisation from methyl and ethyl alcohols. The same products are obtained by hydrolysing amygdalin with barium hydroxide solution, converting the *dl*-amygdalic acid thus produced into its ethyl ester, and acetylation of the latter substance.

The compound described by Campbell and Haworth (T., 1924, **125**, 1337) as ethyl *dl*-hepta-acetylamygdalate is a derivative of *d*-mandelic acid.

In contrast to the previous practice, natural amygdalin, prunasin, and their derivatives which yield lævorotatory mandelic acid when hydrolysed are described as *d*-derivatives, since Freudenberg, Brauns, and Siegel (A., 1923, i, 215) have established the position of lævorotatory mandelic acid among the *d*-α-hydroxy-acids.

H. W.

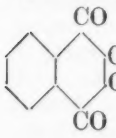
Strophanthin. V. Isomerisation and Oxidation of *iso*-Strophanthidin. W. A. JACOBS and A. M. COLLINS (*J. Biol. Chem.*, 1924, **61**, 387—403; cf. A., 1923, i, 123; this vol., i, 65, 867). —When strophanthidin is treated with cold methyl-alcoholic potassium hydroxide, it is converted quantitatively into α-*iso*strophanthidin, m. p. 255—257°, $[\alpha]_D^{22}$ −34° in methyl alcohol, which is precipitated on pouring the solution into water; more of the substance can be obtained by warming the mother-liquor after acidification to Congo-red. Unlike strophanthidin, it cannot be reduced with hydrogen and palladium, which suggests that isomerisation may involve a shift in the ethylenic linking. It gives an *oxime*, m. p. 236°, which can also be obtained by the action of methyl-alcoholic potassium hydroxide on strophanthidinoxime. On oxidation with sodium hypobromite, α-*iso*strophanthidin gives a mixture of two monobasic, lactonic acids. The greater part of the product is α-iso*strophanthidic acid*, $C_{23}H_{32}O_7$, leaflets with $1H_2O$, m. p. 231—233°, $[\alpha]_D^{23}$ −16·3° in 95% alcohol; the *methyl* ester has a variable melting point, $[\alpha]_D^{20}$ −15° in chloroform; the *benzoate* of the methyl ester has m. p. 230°; the *oxime* of the methyl ester, m. p. 263°. The other *acid*, $C_{23}H_{30}O_7$, was separated by means of its sparingly soluble ammonium salt; it forms needles with $0{\cdot}5H_2O$, m. p. 230°, or anhydrous leaflets, m. p. 254—257°, from hot alcohol; $[\alpha]_D^{23}$ −69° in 95% alcohol. On boiling with sodium hydroxide, the lactone group is hydrolysed with the formation of a dibasic *acid*, $C_{23}H_{32}O_8$, flat needles with $1{\cdot}5H_2O$, m. p. 183°. The *methyl* ester of the lactonic acid has m. p. 253—256°, $[\alpha]_D^{\frac{1}{2}}$ −59·5° in chloroform, and does not form a benzoate or an oxime. On oxidation in ammoniacal solution with potassium permanganate (1 mol. of oxygen), α-*iso*strophanthidic acid gives a dibasic acid, $C_{23}H_{32}O_8$, α-iso*strophanthic acid*, which forms platelets with $1H_2O$, m. p. 232—234°, $[\alpha]_D^{20}$ −8° in methyl alcohol. On heating, this acid loses 1 mol. of carbon dioxide. It can also be obtained directly from *iso*strophanthidin by oxidation in alkaline solution with permanganate (2 mols. of oxygen). The *dimethyl* ester has m. p. 224—225°, $[\alpha]_D^{26}$ −12° in chloroform; the *benzoate* of the dimethyl ester has m. p. 201—203°.

When α-*iso*strophanthidic acid is boiled with dilute sodium hydroxide and then oxidised with permanganate (1 mol. of oxygen) the product consists of a mixture of α-*iso*strophanthic acid and a second isomeric acid which forms needles, m. p. 277—279°, $[\alpha]_D^{25}$ −26° in methyl alcohol, and is identical with the strophanthic acid previously obtained by the oxidation of strophanthidin (this vol., i, 65) and erroneously given the formula $C_{23}H_{30}O_8$. It is now called β-iso*strophanthic acid* and appears to be a stereoisomeride of the α-compound. The strophanthic acid of Feist (A., 1900, i, 555) was probably a mixture of α- and β-*iso*strophanthic acids.

C. R. H.

Constitution of Santonin. A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 10—16).—A reprint of work already published (A., 1907, i, 321; 1908, i, 543). T. H. P.

Mangostin, the Yellow Colouring Matter of the Rind of the Fruit of *Garcinia mangostana*. J. DEKKER (*Rec. trav. chim.*, 1924, **43**, 727—730).—By crystallising from benzene the mixture of colouring matter and resin obtained by extracting the rind with alcohol, mangostin, $C_{16}H_{16}O_4$, is obtained in bright yellow needles, m. p. 176·5—177°. Fusion with alkali gives a product which has the odour of amyl alcohol but, after acidification, of valeric acid. Hence mangostin is possibly methoxyhydroxylapachol (lapachol has the annexed formula; cf. A., 1906, i, 873).



The presence of one methoxyl group is indicated, and the coloration which mangostin gives with ferric chloride points to the presence of a hydroxyl group. Methylation gives *methylmangostin*, yellow crystals, m. p. 122·5—123°, which contains two methoxyl groups and gives a colourless *acetyl* derivative, m. p. 196°. The mangostin obtained in this investigation does not reduce gold and platinum salts; hence the products of Schmid (*Annalen*, 1855, **93**, 83) and of Liechti (*Diss.*, Bern, 1891), which did so, were probably impure. W. E. E.

Preliminary Experiments on Feather Pigments. W. D. BANCROFT (*J. Physical Chem.*, 1924, **28**, 1147—1150).—The red and yellow feather pigments which are or are not easily extracted by alcohol are respectively not fast or fairly fast to light. The solutions in all cases are yellow. The extracted pigment behaves like an acid dye, *i.e.*, it does not dye cotton direct and dyes wool more strongly from an acid than from an alkaline bath. It is adsorbed by alumina. M. B. D.

Pyrylium Compounds. XIII. Reactivity of Methyl Groups in the α- and γ-Positions in Pyrylium Salts. W. DILTHEY and J. FISCHER (*Ber.*, 1924, **57**, [*B*], 1653—1656; cf. Dilthey, A., 1923, i, 699; Buck and Heilbron, T., 1923, **123**, 1395, 2521).—The reactivity of methyl groups in the α- and γ-positions in pyrylium salts is established by their ability to react with aromatic aldehydes. The following salts are thus derived from 4 : 6-diphenyl-2-methylpyrylium compounds: 4 : 6-*diphenyl*-2-*styrylpyrylium perchlorate*, m. p. 235°; 4 : 6-*diphenyl*-2-p-*methoxystyrylpyrylium perchlorate*, m. p. 228—229°, and the additive *compound* of the chloride with ferric chloride, m. p. 198°; 4 : 6-*diphenyl*-2 : 4′-*hydroxystyrylpyrylium perchlorate*, m. p. 254°, and the *ferric* compound, m. p. 172°; 4 : 6-*diphenyl*-2 : 2′-*hydroxystyrylpyrylium perchlorate*, m. p. 248°, and the *ferric* salt, m. p. 174°; 4 : 6-*diphenyl*-2-β-*styrylvinylpyrylium perchlorate*, m. p. 255°, and the *ferric* compound, m. p. 236°. 2 : 6-Diphenyl-4-methylpyrylium salts yield the following compounds: 2 : 6-*diphenyl*-4-*styrylpyrylium perchlorate*, m. p. 254—255°; 2 : 6-*diphenyl*-4-p-*methoxystyrylpyrylium perchlorate*, m. p. 272°; 2 : 6-*diphenyl*-4-p-*hydroxystyrylpyrylium perchlorate*, m. p. 265°; 2 : 6-*diphenyl*-4-o-*hydroxystyrylpyrylium perchlorate*, m. p. 243—244°; 2 : 6-*diphenyl*-4-β-*styrylvinylpyrylium perchlorate*, m. p. 240°.

In reply to Schneider and Ross (A., 1923, i, 1111), it is admitted that the formation of 4 : 6-diphenyl-2-methylpyrylium salts from acetophenone and acetic anhydride may occur through the intermediate formation of dypnone, but experimental evidence is adduced in favour of the view that benzoylacetone is more probably an intermediate product. H. W.

Sulphur as the Bridge Atom in the Middle Ring of some Anthracene Derivatives. A. Bistrzycki and A. Traub (*Helv. Chim. Acta*, 1924, **7**, 935—944; cf. A., 1922, i, 268).—In warm glacial acetic acid solution, hydrogen chloride causes *p*-tolualdehyde and thiobenzilic acid to condense almost quantitatively to give 4 : 4-*diphenyl*-2-p-*tolyl*-1 : 3-*oxthiophan*-5-*one*, prisms, m. p. 100—100·5°. Sulphuric acid converts this substance into 9-*phenyl*-2-*methyl*-9 : 10-*dihydro*mesothioanthracene, greenish-yellow needles, m. p. 99·5—100·5°. Neither alcoholic phenylhydrazine nor boiling 10% alcoholic sodium hydroxide solution affects the substance, so that the sulphur cannot be bound as in a thioketone. Distilled with zinc dust under the conditions in which phenyldihydro*meso*thioanthracene gives phenylanthracene, the present substance gives no solid product. At a higher temperature 2-methylanthracene is obtained.

Reduction in glacial acetic acid solution by zinc dust and hydrochloric acid gives 1-*phenyl*-3-p-*tolylthiophthalan*, needles, m. p. 103—104°. Oxidation in boiling glacial acetic acid solution by 4% potassium permanganate solution yields 2-*p*-toluoylbenzophenone. The condensation of thiobenzilic acid and cuminaldehyde gives 4 : 4-*diphenyl*-2-*cumenyl*-1 : 3-*oxthiophan*-5-*one*, m. p. 100—100·5°. From *o*-chlorobenzaldehyde 4 : 4-*diphenyl*-2-o-*chlorophenyl*-1 : 3-*oxthiophan*-5-*one*, m. p. 105·5°, is obtained, and is converted by sulphuric acid into 4-*chloro*-9-*phenyl*-9 : 10-*dihydro*mesothioanthracene, green prisms, showing marked triboluminescence, m. p. 89°. Alcoholic ammonium hydroxide at 220—230° has no action on this compound. *m*-Chlorobenzaldehyde gives (quantitatively) 4 : 4-*diphenyl*-2-m-*chlorophenyl*-1 : 3-*oxthiophan*-5-*one* (m. p. 83—84°), and thence (probably) 3-*chloro*-9-*phenyl*-9 : 10-*dihydro*mesothioanthracene (m. p. 102—103·5°). Whilst 2-*o*-nitrophenyl-4 : 4-diphenyl-1 : 3-oxthiophan-5-one could not be converted into an anthracene derivative, 2-*m*-nitrophenyl-4 : 4-diphenyl-1 : 3-oxthiophan-5-one gives 3-*nitro*-9-*phenyl*-9 : 10-*dihydro*mesothioanthracene (m. p. 151° indef., depending on rate of heating). The following condensation products of thiobenzilic acid are all obtained in good yield by the usual method, but they do not give the corresponding *meso*thioanthracene derivatives: 4 : 4-*diphenyl*-2-p-*nitrophenyl*-1 : 3-*oxthiophan*-5-*one* (m. p. 148°), 4 : 4-*diphenyl*-2-p-*dimethylaminophenyl*-1: 3-*oxthiophan*-5-*one* (m. p. 124° decomp.), 4 : 4-*diphenyl*-2-(mp-*methylenedioxyphenyl*)-1 : 3-*oxthiophan*-5-*one* (m. p. 119·5°), 1 : 4-*di*-2(5-*keto*-4 : 4-*diphenyltrihydro*-1 : 3-*oxthienyl*)*benzene* (m. p. 195—196°). W. E. E.

Naphthathioindoxyls. R. Tobler, R. Stocker, J. Müller, and A. Bucher (U.S. Pat. 1492054).—Treatment of thionaphtho-

isatin compounds in alkaline solution with a monohalogen acid, elimination of carbon monoxide, and ring closure by condensation yields naphthothioindoxyls. The following compounds are mentioned: *Naphthalene-1-thioglyoxylic acid*, m. p. 171—172°; *naphthalene-1-thioglycol-2-carboxylic acid*, m. p. 144—145°; 1 : 2-*naphthothioindoxyl*; 2 : 1-*naphthothioindoxyl*; 4-*chloro*-1 : 2-*naphthothioindoxyl*, m. p. 165° (5-*chloro*-, m. p. 176°); 5-*chloro*-2 : 1-*naphthothioindoxyl*, m. p. 146° (5-*bromo*-, m. p. 170°; 8-*chloro*-, m. p. 179°; 7-*chloro*-, m. p. 155°); 1-*chloro*-2 : 3-*naphthothioindoxyl* (*acetyl* derivative, m. p. 106°); 1-*bromo*-2 : 3-*naphthothioindoxyl*, m. p. 155°.

CHEMICAL ABSTRACTS.

Indigotin Group. V. Derivatives of "Thioindigo." T. POSNER and E. WALLIS (*Ber.*, 1924, **57**, [*B*], 1673—1681; cf. Posner and Heumann, A., 1923, i, 953; Posner and Kemper, this vol., i, 1237).—The assumption made previously that the action of nitrous fumes on indigotin results in the replacement of the imino-hydrogen atoms by the nitroso group is confirmed indirectly by the observation that bisoxythionaphthen is only slowly attacked by this reagent, whereby it is converted into thionaphthenquinone, $C_6H_4<^{CO}_{S}>CO$, m. p. 121°.

Bisoxythionaphthen is slowly oxidised by nitric acid (*d* 1·4) at the atmospheric temperature to the corresponding *monosulphoxide*, $C_6H_4<^{CO}_{SO}>C{:}C<^{CO}_{S}>C_6H_4$, m. p. above 300°, which appears to be identical with the substance described by Bezdrik, Friedländer, and Koeniger (A., 1908, i, 200), and by Danaila (A., 1910, i, 411). The compound is readily reduced by sodium hyposulphite and sodium hydroxide to the dihydro substance, which, however, is oxidised by air to bisoxythionaphthen. Addition of benzoyl chloride to the vat yields the *dibenzoyl* derivative, $C_6H_4<^{C(OBz)}_{SO}>C{\cdot}C<^{C(OBz)}_{S}>C_6H_4$, m. p. 214—215°, whereas the action of benzoyl chloride on the sulphoxide in the presence of boiling pyridine leads to the production of 3 : 3′-*bisbenzoxythionaphthen*, m. p. 226°, which is also prepared by the action of benzoyl chloride on the hyposulphite vat from bisoxythionaphthen or on the latter dissolved in boiling pyridine. The sulphoxide is transformed by reductive acetylation with acetic anhydride into 3 : 3′-*bisacetoxythionaphthen*, m. p. 240°, which is obtained similarly from bisoxythionaphthen. Warm sodium hydroxide solution converts the sulphoxide into thionaphthenquinone.

Bisoxythionaphthen is transformed by nitric acid (94%) in the presence of glacial acetic acid into the corresponding *sulphone*, $C_6H_4<^{CO}_{SO_2}>C{:}C<^{CO}_{S}>C_6H_4$, m. p. above 300°. The *dibenzoyl* derivative, m. p. 228—229° (decomp.), and the *diacetyl* compound, m. p. 206°, of the corresponding dihydro product are described. The monosulphone is transformed by sodium hydroxide solution (15%) into thionaphthenquinone and *thionaphthen-*

quinone-S-*dioxide*, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>CO$, m. p. 265°, which is reduced by zinc dust and glacial acetic acid to 3-hydroxy-1-dioxythionaphthen, m. p. 142° (cf. Lanfry, A., 1913, i, 193).

6 : 6′-Diethoxybisoxythionaphthen is converted in the usual manner into the *dibenzoyl* derivative, m. p. 260°, and the *diacetyl* derivative, m. p. 232° (decomp.), of the corresponding dihydro compound. H. W.

Angostura Alkaloids. II. Synthesis of Galipine. E. Späth and H. Eberstaller (*Ber.*, 1924, **57**, [*B*], 1687—1690; cf. Späth and Brunner, this vol., i, 1226).—4-Methoxy-2-methylquinoline condenses with 3 : 4-dimethoxybenzaldehyde in the presence of zinc chloride at 105° to yield 4-*methoxy*-2-β-3′ : 4′-*dimethoxyphenylethinenylquinoline* [*hydrochloride*, m. p. 174—176° (decomp.)], which is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2-β-3′ : 4′-dimethoxyphenylethylquinoline, $OMe{\cdot}C_9H_5N{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, m. p. 113·5° (*picrate*, m. p. 194°); the base is identical with natural galipine.

The isolation of the angostura alkaloids is conveniently effected by extraction of the bark with ethyl alcohol and concentration of the extract in a vacuum to a viscous syrup. The dark residue is treated with sodium hydroxide solution (25%), which dissolves the bulk of the coloured impurities and enables the alkaloids to be extracted with ether. The ethereal extract is repeatedly treated with dilute hydrochloric acid (1%), whereby cusparine and galipine are dissolved, whilst the more feebly basic alkaloids are removed from the remaining ethereal solution by hydrochloric acid (10%). Cusparine is separated from its mixture with galipine as the sparingly soluble oxalate. H. W.

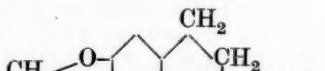
Synthesis of ψ-Pelletierine. R. C. Menzies and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 2163—2168).—Aqueous solutions of calcium acetonedicarboxylate, glutardialdehyde, and methylamine were mixed and kept for 24 hours. The mixture was then acidified (to Congo-red) with hydrochloric acid, boiled to eliminate carbon dioxide, cooled, rendered alkaline, and the calcium removed as oxalate. Extraction with ether then gave an oil which was distilled in a high vacuum. The distillate afforded a sparingly-soluble *picrate*, which, after recrystallisation from water, decomposition with sodium hydroxide, and extraction with ether etc. afforded a crystalline base. Recrystallisation from light petroleum yielded crystals, m. p. 48·5°, identical with ψ-pelletierine. *Dipiperonylidene-ψ-pelletierine*, m. p. 226—227°, forms yellow, microscopic plates or prisms.

Adipdialdehyde similarly gave rise to an oily *base* possessing properties to be expected of a homo-ψ-pelletierine. It yielded a *dipiperonylidene* derivative and a *methiodide*. F. G. W.

Oxidation of Substituted 1-Benzyl-3 : 4-dihydro*iso*quinolines and a Synthesis of Papaveraldine. J. S. Buck, R. D. Haworth, and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 2176—2185).—When 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-1-

benzyl-3 : 4-dihydro*iso*quinoline (cf. Haworth, Perkin, and Rankin, this vol., i, 1098) is exposed to the air in alcoholic solution, 3′ : 4′-*dimethoxy*-1-*benzoyl*-6 : 7-*methylenedioxy*-3 : 4-*dihydro*isoquinoline (I), m. p. 151° [*hydriodide*, m. p. 209—211°; *oxime*, m. p. 232° (decomp.)], is obtained. This, and its homologues, develop a brilliant green coloration when boiled with acetic anhydride. Reduction with tin and hydrochloric acid affords the corresponding 1 : 2 : 3 : 4-tetrahydro*iso*quinoline derivative (*loc. cit.*, 1099). Treatment with benzoyl chloride yields the *benzoyl* derivative (probably II; cf. Reissert, A., 1905, i, 925), pale yellow needles, m. p. 158°, from which (I) is re-formed on boiling with 40% sulphuric acid. When (I) is heated with methyl-alcoholic potassium hydroxide, it is oxidised to 3′ : 4′-*dimethoxy*-1-*benzoyl*-6 : 7-*methylenedioxy*isoquinoline, m. p. 208° [*picrate*, m. p. 206—207° (decomp.); *oxime*,

(I.)

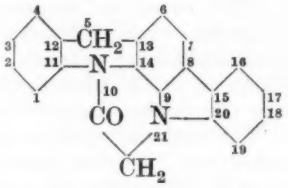


(II.)

m. p. 260° (decomp.)]. 3′ : 4′-*Methylenedioxy*-1-*benzoyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline, prisms, m. p. 151—152°, is obtained similarly to (I). The *hydriodide*, m. p. 192°; *picrate*, m. p. 227° (decomp.) after softening at 215°; and *oxime*, m. p. 223—224°, are described. It yields the tetrahydro*iso*quinoline derivative on reduction, and forms a pale yellow *benzoyl* derivative (see II), m. p. 151°, which yields an amorphous *monoxime*, and an o-*nitrobenzoyl* derivative, m. p. 175—176°. The action of aqueous permanganate, or of methyl-alcoholic potassium hydroxide, affords 3′ : 4′-*methylenedioxy*-1-*benzoyl*-6 : 7-*dimethoxy*isoquinoline, m. p. 199—200° [*picrate*, m. p. 243°; *oxime*, m. p. 263—264° (decomp.)], together with, in the latter case, a *substance*, $C_{19}H_{17}O_6N$, m. p. 294—296°. 6 : 7 : 3′ : 4′-*Tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline was obtained as an oil (*picrate*, m. p. 168°) by the action of phosphoryl chloride in toluene on homoveratroylhomoveratrylamine. It was oxidised as above to 6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline, a cream-coloured powder, m. p. 190—191°. The *hydrochloride*, $C_{20}H_{21}O_5N,HCl,H_2O$, yellow, m. p. 183°; *hydriodide*, orange, m. p. 186° (decomp.); *oxime*, m. p. 247—248° (decomp.); and *benzoyl* derivative, pale yellow, m. p. 160°, are described. When warmed with methyl-alcoholic potassium hydroxide, the base yielded 6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzoyl*isoquinoline, m. p. 208°, identical with papaveraldine.

F. G. W.

Strychnine and Brucine. II. G. R. Clemo, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 1751—1804).—Perkin and Robinson (T., 1910, **97**, 305) have suggested that the strychnine molecule possessed the carbon–nitrogen skeleton of an anhydro-(5 : 10-dihydro)-acrindoline-21-acetic acid (annexed formula, the novel numbering of which should be noted). Substances having this skeleton have now been synthesised. The immediate aim of the work was to reproduce if possible either deoxystrychnine or dihydrostrychnoline (Tafel, A., 1892, 1012) but this has not been achieved.



When 9-amino-5 : 10-dihydroacridine (see below) is treated with ethyl chloroacetate and the product hydrolysed, *anhydro*-5 : 10-*dihydroacridine*-9-*aminoacetic acid*, m. p. 168° (a crystallographic description is given), is obtained [*acetyl* derivative, m. p. 174—175°; *nitroso* derivative, m. p. 167° (decomp.)]. When the nitroso derivative is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone, condensation takes place and *anhydro*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*-21-*acetic acid*, yellow plates, m. p. 206°, is formed. This affords the corresponding *acid*, an amorphous substance, when treated with methyl-alcoholic potassium hydroxide, but the product is not wholly reconverted into the anhydride by the action of ethyl-alcoholic hydrochloric acid, some being also oxidised to *ethyl* 16 : 17 : 18 : 19-*tetrahydroacrindoline*-21-*acetate*, m. p. 172° (see below). Strychnic acid does not behave in a similar way. When the above anhydride is reduced electrolytically in alcoholic sulphuric acid suspension—and only by this means—it affords 21-β-*hydroxyethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, an amorphous, gummy substance which yields a crystalline *diacetyl* derivative, m. p. 235°. When the latter is hydrolysed by methyl-alcoholic potassium hydroxide it is presumably simultaneously oxidised as the product has the properties of an acridine derivative (fluorescent solution in sulphuric acid). In its formation and acetylation the parent substance resembles tetrahydrostrychnine (Tafel, *loc. cit.*), but not in this other behaviour.

Anhydrohexahydroacrindoline-21-acetic acid suffers partial reduction when it is distilled over zinc dust at 20 mm. and by repeated treatment is thus converted into 10 : 21-*etheno*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, a yellow substance, m. p. 181—182°, which gives red salts (the *hydrochloride* and *sulphate* are described). This compound is formulated as an etheno compound, and not as an *N*-vinyl derivative, for reasons that are discussed in detail and are based on evidence published elsewhere (cf. this vol., i, 1345). As a by-product, formed by oxidation in the later operations, 16 : 17 : 18 : 19-*tetrahydroacrindoline*-21-*acetic acid*, an amorphous substance, is obtained; its *ethyl* ester forms orange prisms, m. p. 172°. From the etheno derivative, by reduction with sodium amalgam in presence of an excess of carbon dioxide, 10 : 21-*ethano*-

5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, yellow prisms, m. p. 209°, is produced; in this, as it yields no acetyl derivative, the 10 : 21 bridge is still intact. Further reduction, by electrolysis of an alcoholic sulphuric acid suspension at 35—45°, converts the ethano compound into what is most probably 21-*ethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, m. p. 127° (yielding an *acetyl* derivative, m. p. 173°, and a *sulphate* which is decomposed by ammonia), together with 21-*ethyl*-5 : 6 : 7 : 8 : 9 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*dodecahydroacrindoline*, a strongly basic resinous substance—the *sulphate*, m. p. 230° (decomp.), is not decomposed by ammonia—yielding an *acetyl* derivative, $C_{21}H_{27}N_2Ac$, which also is resinous. The ethenotetrahydro, ethano- and ethyl-octahydro, and the ethyldodecahydro compounds do not exhibit the physiological properties characteristic of strychnine.

Compounds having the complete "strychnine skeleton" were synthesised only in the above way; earlier abortive attempts resulted in the production of the following compounds, some of which, indeed, were made use of in the experiments described above.

2′-Nitrodiphenylamine-6-carboxylic acid, obtained from anthranilic acid and *o*-chloronitrobenzene, is converted by sulphuric acid at 100° into 9-nitroacridone (cf. Ullmann, A., 1907, i, 842), the 3(?)-*sulphonic acid* of which yields a *chloride*, m. p. 270—274°. When 9-nitroacridone is reduced with ammonium sulphide 9-aminoacridone is obtained, and this with ethyl bromoacetate affords (eventually) *acridone*-9-*aminoacetic acid*, a gelatinous substance; the *methyl* ester forms yellow prisms, m. p. 237—238°, and affords a *nitroso* derivative, decomp. 180°; the *ethyl* ester forms yellow needles, m. p. 195°, and affords a *nitroso* derivative, m. p. 185—186° (decomp.). The latter, the nitroso ethyl ester, undergoes a condensation when it is reduced with zinc and acetic acid in presence of *cyclo*hexanone, but in the reaction the carbethoxymethyl group is wholly removed, and the product is not the expected anhydroketohexahydroacrindolineacetic acid, but 5-*keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, dull yellow prisms, m. p. above 380° (the *hydrochloride*, *hydrobromide*, *nitrate*, and *sulphate*, all bright red substances, are described). This substance is also obtained (and so its constitution verified) as follows: 9-aminoacridone is converted by the action of nitrous acid into *acridonediazole*, m. p. 266°, and this readily yields the desired product when it is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone.

The above keto compound, when reduced by sodium amalgam and an excess of carbon dioxide, affords 5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, m. p. 187—205° (the *hydrochloride* and *sulphate* are red), which is oxidised by boiling its alcoholic solution in contact with air to 16 : 17 : 18 : 19-*tetrahydroacrindoline*, m. p. 230—231° (this also forms red salts: *hydrochloride*, *sulphate*, and *picrate*).

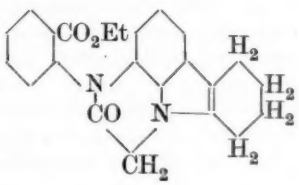
2′-*Aminodiphenylamine*-6-*carboxylic acid*, m. p. 210° (*hydrochloride*, m. p. 260°), is obtained by reducing the nitro compound mentioned above with ferrous sulphate and ammonia. This acid

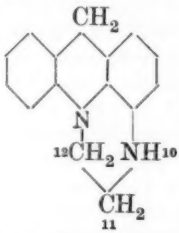
is converted at its m. p. into the *anhydro* derivative (*2′-aminophenylanthranil* ?), m. p. 250° [*acetyl* derivative, m. p. 248°; *nitroso* derivative, m. p. 202° (decomp.)]. The aminodiphenylaminecarboxylic acid interacts with phenanthraquinone to afford *flavinduline-o-carboxylic acid*, m. p. 310° (decomp.). It also yields, when treated with nitrous acid, 1-o-*carboxyphenyl*-1 : 2 : 3-*benztriazole*, m. p. 217° (decomp.); this product resisted all attempts to convert it into acridonediazole or into an indole derivative.

From *o*-phenylenediamine and *o*-chlorobenzoic acid, *6-carboxydiphenylamine-2′-o-aminobenzoic acid* (*s-di-o-carboxyphenyl-o-phenylenediamine*), m. p. 258°, is obtained; this is decomposed, when heated under diminished pressure, and converted into *s-diphenyl-o-phenylenediamine*, m. p. 109°, b. p. 280—290°/40 mm., the *diacetyl* derivative of which has m. p. 281° [Wieland's base (A., 1913, i, 1386) is most probably *o*-aminotriphenylamine].

When 2′-aminodiphenylamine-6-carboxylic acid is treated with sodium formaldehyde-bisulphite followed by potassium cyanide and, finally, by sodium hydroxide, *6-carboxydiphenylamine-2′-aminoacetic acid*, m. p. 212°, is produced; this, by the action of alcoholic hydrochloric acid, is converted into the ester of the anhydro derivative, namely, *anhydro-6-carbethoxydiphenylamine-2′-aminoacetic acid*, m. p. 153°, of which the *nitroso* derivative (m. p. 117°) undergoes the usual condensation when reduced in presence of *cyclo*hexanone, yielding *anhydro-8-o-carbethoxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole-9-acetic acid* (I), yellow prisms,

(I.)





(II.)

m. p. 172°; the dibasic acid of which this is the anhydro ester, namely, 8-o-*carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole-9-acetic acid*, has m. p. 243° (*acetyl* derivative, m. p. 250°) and when it is heated with sulphuric acid gives no acrindoline derivative but only *anhydro-8-o-carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole-9-acetic acid*, m. p. about 255°.

9-Amino-5 : 10-dihydroacridine, m. p. 114°, is obtained either through *9-nitrothioacridone*, m. p. 236° (from the nitroacridone and phosphorus pentasulphide), or, better, by reducing the nitroacridone itself with sodium amalgam in presence of an excess of carbon dioxide. Its *acetyl* derivative has m. p. 177°; when this is oxidised with potassium dichromate *9-acetamidoacridine*, m. p. 117°, is obtained, and hydrolysis with boiling 60% sulphuric acid then affords *9-aminoacridine*, orange prisms, m. p. 105—106° (*hydrochloride*, m. p. 234°, decomp.). The latter interacts with ethyl chloroacetate to afford *ethyl acridine-9-aminoacetate*, m. p. 109°

(the *acid* has m. p. about 185°, decomp.), the *nitroso* derivative (m. p. 115—117°) of which is remarkable in giving no condensation product when it is reduced with zinc and acetic acid in presence of *cyclo*hexanone.

The *toluene*-p-*sulphonyl* derivative, m. p. 169—170° (*hydrochloride*, m. p. 242°), of 9-aminoacridine interacts with ethyl toluene-*p*-sulphonate to yield the *toluene*-p-*sulphonyl* derivative (m. p. 175—176°) of 9-*ethylaminoacridine*, orange-red plates, m. p. 65° (*acetyl* derivative, m. p. 95°).

Anhydro-5 : 10-dihydroacridine-9-aminoacetic acid (see above) is converted by the action of phosphorus pentachloride into a *compound*, $C_{30}H_{23}O_3N_4ClP$, m. p. 175—178°.

When anhydrodihydroacridineaminoacetic acid is electrolytically reduced it yields what is probably 11 : 12-*dihydroacridoxaline* (II), a gummy substance with a pronounced irritant action on the skin. The *acetyl* derivative of this compound has m. p. 152°, but even when this is hydrolysed the parent reappears as a gum. It was thought at first that this product was the ethylaminoacridine described above (there being the two possibilities), but the independent preparation showed that this was not so.

The *toluene*-p-*sulphonyl* derivative (m. p. 190—191°) of 9-amino-5 : 10-dihydroacridine affords a β-*chloroethyl* derivative (m. p. 147—148°) when it is treated with β-chloroethyl toluene-*p*-sulphonate, but this resists condensation to form a dihydrocarboxaline ring. The analogous β-*hydroxyethyl* derivative (m. p. 154—155°) is obtained when ethylene chlorohydrin is used, and this also will not undergo intramolecular condensation. When it is oxidised in hot acetic acid solution with potassium dichromate, the *toluene*-p-*sulphonyl* derivative (m. p. 156°) of the corresponding acridine is obtained, and this affords the parent compound, namely, 9-β-*hydroxyethylaminoacridine*, m. p. 109—110°, when hydrolysed with boiling 60% sulphuric acid. This is reduced by treatment with sodium amalgam in presence of much carbon dioxide to 9-β-*hydroxyethylamino*-5 : 10-*dihydroacridine*, m. p. 122—123° (*diacetyl* derivative, m. p. 148°; partial hydrolysis affords the *monoacetyl* derivative, m. p. 147—148°); fruitless experiments were made to close the dihydrocarboxaline ring in this compound, using a variety of condensing agents.

When the potassium compound of the toluene-*p*-sulphonyl derivative of 9-amino-5 : 10-dihydroacridine and bromodimethylacetal are heated together at 100° in methyl-alcoholic solution the *dimethylacetalylsulphonyl* derivative, m. p. 121°, is obtained; subsequent treatment with ethyl-alcoholic hydrochloric acid produced an amorphous substance.

9-Amino-5 : 10-dihydroacridine and bromodimethylacetal (with sodium acetate, and a little copper, in alcoholic solution) afford eventually 9-*aminoacridine dimethylacetal*, m. p. 87°, which is converted by reduction with sodium amalgam into the corresponding *derivative* of the 5 : 10-dihydroacridine, m. p. 63—64°.

When the aminodihydroacridine interacts with ethyl bromoacetate *ethyl anhydro*-5 : 10-*dihydroacridine*-9-*aminodiacetate*, m. p.

154—156°, is obtained, the parent *acid* of which has m. p. 192° (after losing 1 mol. MeOH—of crystallisation ?). This acid decomposes when heated at 20 mm., yielding a distillate consisting of *anhydro*-5 : 10-*dihydroacridine* 9-*methylaminoacetic acid*, m. p. 131—132°.

6-*Nitro*-9-*methylacridone* (m. p. above 300°, prepared from 4-nitrotolylanthranilic acid) yields, when reduced with sodium amalgam in the manner indicated above, 6-*amino*-9-*methyl*-5 : 10-*dihydroacridine*, orange prisms, m. p. 118°, and 9-chloroacridone (Ullmann, *loc. cit.*) similarly affords 9-*chloro*-5 : 10-*dihydroacridine*, needles, m. p. 79° (unstable), or prisms, m. p. 90—91° (stable form).

W. A. S.

Determination of Constitution by Spectroscopic Methods. Constitution of Amino-acids. I. H. Ley and F. H. Zschacke (*Ber.*, 1924, **57**, [*B*], 1700—1707).—Comparison of the absorption curves of piperidinoacetic acid with those of its sodium salt, hydrochloride, ethyl ester, and sodium acetate shows that it is impossible that the acid exists in the normal form, $C_5H_{10}N{\cdot}CH_2{\cdot}CO_2H$, since the absorption of the acid is not intermediate between that of the sodium salt and the ester. The close identity of the absorption curves of the acid and sodium acetate suggests further that the normal form cannot be present to an appreciable extent. The choice between the constitutions indicated by the schemes $R{<}\begin{matrix}NH_2\cdots H\\ CO\text{——}O\end{matrix}$ and $\cdot NH_3{\cdot}R{\cdot}CO_2'$ cannot be effected on the bases of optical measurements. In the case of aromatic amino-acids, such as *o*-aminobenzoic acid and the acids of the pyridine series, the neutral form greatly predominates.

H. W.

Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen.—(See i, 1299.)

6-Methoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. L. Helfer (*Helv. Chim. Acta*, 1924, **7**, 945—950).—The initial stages in the synthesis of this compound are described as follows: *m*-nitrobenzaldehyde → *m*-aminobenzaldehyde → *m*-hydroxybenzaldehyde → *m*-methoxybenzaldehyde → *m*-anisylacrylic acid → *m*-anisylpropionic acid → *methyl* m-*anisylpropionate* (m. p. 29—30°, b. p. 150—152°/14 mm.) → m-*anisylpropionamide* (m. p. 56°, b. p. 218—219°/9 mm.) ⇌ β-m-*anisylethylamine* (b. p. 247—248° or 122—123°/7 mm.). The last substance is a strong base forming a *carbonate*; *hydrochloride*, m. p. 145—146°; *picrate*, m. p. 134°; and *chloroplatinate*, m. p. 204—205° (decomp.). The action of formaldehyde on β-*m*-anisylethylamine gives β-m-*anisylethylmethylene-amine*, a viscous oil. Evaporated to dryness with hydrochloric acid, this gives the *hydrochloride* of 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline. The latter is a strong base (b. p. 143—144°/6 mm.), forming a crystalline *carbonate*; *hydrochloride*, m. p. 233—234°; *picrate*, m. p. 173—174° (decomp.); *chloroplatinate*, orange-red, m. p. 198°;

and *nitrosoamine*, a yellow oil. When the base is oxidised by alkaline permanganate, 4-methoxyphthalimide (m. p. 231°) is obtained together with some 4-methoxyphthalic acid (T., 1907, **91**, 103). W. E. E.

Isatin and Related Compounds. VI. 5-Iodoisatin and 5 : 5′-Di-iodoindigotin. W. Borsche, H. Weussmann, and A. Fritzsche (*Ber.*, 1924, **57**, [*B*], 1770—1775).—*5-Iodoisatin*, m. p. 264—265°, is prepared by the action of iodine monochloride on a solution of isatin in glacial acetic acid or by the action of concentrated sulphuric acid on p-*iodo-oximinoacetanilide*, $C_6H_4I{\cdot}NH{\cdot}CO{\cdot}CH{:}N{\cdot}OH$, m. p. 180—182° (prepared from *p*-iodoaniline, hydroxylamine, and chloral hydrate). *5-Iodoisatin-3-hydrazone*, decomp. 240° after becoming discoloured at 170°, is described. *5-Iodo-1-methylisatin*, m. p. 175°, is obtained by methylation of 5-iodoisatin with methyl sulphate and sodium hydroxide, or from 1-methylisatin and iodine chloride. 5-Iodoisatin is transformed by acetone in the presence of aqueous-alcoholic potassium hydroxide solution into 6-*iodo*-2-*methylquinoline*-4-*carboxylic acid*, m. p. 290°, which passes at 300° into 6-*iodo*-2-*methylquinoline*, m. p. 107—108° (*picrate*, m. p. 194—195°). Similarly, acetophenone and 5-iodoisatin give 6-iodo-2-phenylquinoline-4-carboxylic acid, m. p. 249—250°, from which 6-*iodo*-2-*phenylquinoline*, m. p. 143—144°, is derived. *6-Iodo-2-hydroxyquinoline-4-carboxylic acid*, m. p. above 320°, is converted by a solution of phosphorus pentachloride in phosphoryl chloride into a mixture of 2-*chloro*-6-*iodoquinoline*-4-*carboxylic acid*, m. p. 215—216°, and 6-*iodo*-2-*hydroxyquinoline*-4-*carboxylyl chloride*, m. p. 265—266°.

5-Iodoisatin chloride, m. p. 226—228°, prepared from iodoisatin and phosphorus pentachloride in the presence of benzene, is transformed by heating with aniline into *5-iodo-2-aniloisatin*, m. p. 223—224°, and thence by the action of ammonium sulphide and hydrogen sulphide into 5 : 5′-*di-iodoindigotin*.

5-Iodoanthranilic acid, m. p. 212—214° (decomp.), is conveniently prepared by the action of iodine monochloride on anthranilic acid dissolved in glacial acetic acid. It is converted by acetic anhydride into *5-iodo-2-acetamidobenzoic acid*, m. p. 241—242°. Attempts to prepare the latter compound by the direct iodination of acetamidobenzoic acid yielded a mixture of unchanged material and 3 : 5-*di-iodoanthranilic acid*, m. p. 232—233°; if a larger proportion of iodine chloride is used, 2 : 4 : 6-tri-iodoaniline, m. p. 186°, is also produced. *5-Iodo-2-cyanomethylaminobenzoic acid*,

$$CN{\cdot}CH_2{\cdot}NH{\cdot}C_6H_3I{\cdot}CO_2H,$$

m. p. 217°, is obtained together with an unidentified *substance*, m. p. 184—186°, by the action of potassium cyanide and formaldehyde on 5-iodoanthranilic acid in aqueous solution. It is hydrolysed by 3*N*-sodium hydroxide solution to *5-iodo-2-carboxymethylaminobenzoic acid*, m. p. 207—208°, which is more conveniently obtained from phenylglycine-*o*-carboxylic acid and iodine chloride. It appears to lose a part of the iodine when fused with potassium hydroxide. H. W.

Transformation of Isatogen Derivatives into Isatins. P. RUGGLI and W. LEONHARDT (*Helv. Chim. Acta*, 1924, **7**, 898—907).—The by-product previously obtained (this vol., i, 1106) from the action of acetic anhydride and sulphuric acid on 6-nitro-2-phenylisatogen varies according to the proportion of sulphuric acid. It is yellow (for additive products of nitrophenylisatogen and acetic anhydride, see below) for acid percentages below 3, and red when the percentage is 3 to 6, and then consists chiefly of 6-*nitro*-1-*phenylisatin*, m. p. 232° (*ammonium*, *potassium*, *barium*, and *silver* salts described; *methyl ether*, reddish-gold leaflets, m. p. 82°). The barium salt, when heated in acetic acid solution, affords 4-*nitro*-1-*phenylisatic acid*, yellow crystals, m. p. 288—290° (decomp.). With *o*-phenylenediamine, the nitrophenylisatin affords 6-*nitro*-1-*phenylindophenazine*, yellow needles, m. p. above 310° (decomp.). The *oxime* of the nitroisatin forms yellow needles, m. p. 227—230° (decomp.), and is converted by diazomethane into the *methyl ether*, golden-yellow tablets, decomp. 170—175°. The corresponding *hydrazone* forms yellow leaflets, m. p. 220—225° (decomp.), and the β-*phenylhydrazone*, brick-red needles, m. p. 238° (decomp.). The latter, when heated with excess of phenylhydrazine, gives 6-*amino*-1-*phenylisatin*-β-*phenylhydrazone*, red needles, m. p. 213° (*diacetyl* derivative, orange-yellow needles, m. p. 255—256°). From the above nitrophenylisatin mother-liquors, 4-*nitrobenzoylanthranil* (m. p. 179°) and 4-*nitrobenzoylanthranilic* acid (m. p. 252°) were also obtained. By treatment with acetic anhydride the latter is converted into the former.

Nitrophenylisatogen forms a labile *additive* compound (yellow needles, decomp. 65—70°) with acetic anhydride (1 mol.) when treated with a mixture of the latter with sulphuric acid. W. E. E.

Fission of the Pyridine Nucleus during Reduction. B. D. SHAW (*J. Chem. Soc.*, 1924, **125**, 1930—1934).—When pyridine is reduced with sodium and aqueous alcohol (95%) instead of absolute alcohol, little or no piperidine is formed, but ammonia is evolved and a resinous nitrogen-free product is obtained, with traces of a volatile oil, possibly pentamethylene oxide. Simple derivatives of pyridine also suffer this disruption (cf. Mumm and Brodersen, this vol., i, 82). Ammonia is readily given off when 2-stilbazole is similarly reduced and the product, after repeated treatment to ensure complete conversion, consists chiefly of 2-β-*phenylethyltetrahydropyran*, m. p. 77°. Quantitative experiments with pyridine indicate that the scission takes place at the dihydro stage of the reduction. W. A. S.

Vinyl Derivatives, especially of Carbazole and Tetrahydrocarbazole, and their Behaviour with Acids. G. R. CLEMO and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 1804—1814).—By interaction of toluene-*p*-sulphonanilide and β-chloroethyl toluene-*p*-sulphonate *toluene*-p-*sulphon*-β-*chloroethylanilide*, m. p. 76°, is obtained. When treated with potassium iodide in hot amyl alcohol, it affords the β-*iodo* analogue, m. p. 81—82°; with diethylamine in alcohol at 160° it yields a product from which,

by hydrolysis, β-*diethylaminoethylaniline*, b. p. 163°/17 mm., is obtained; similarly, with *o*-chloroaniline, potassium carbonate and a little copper powder, the *toluene*-p-*sulphonyl* derivative, m. p. 110°, of β-o-*chlorophenylaminoethylaniline*, b. p. 238—242°/20 mm. (*hydrochloride*, m. p. 185°), is produced. Further, treatment with methyl-alcoholic potassium hydroxide effects the conversion into *toluene*-p-*sulphonvinylanilide*, m. p. 96—97°; this unites with bromine to form an unstable *dibromo* compound, which is converted by warm methyl-alcoholic potassium hydroxide into *toluene*-p-*sulphon*-β-*bromo*-α-*methoxyethylanilide*, m. p. 78—79°. The vinyl derivative is readily decomposed when it is treated with dilute sulphuric acid, the parent anilide and acetaldehyde being formed. This agrees, and so do the observations described below, with the results obtained by other investigators (cf. *e.g.*, von Braun and Kirschbaum, A., 1920, i, 154) of the behaviour of *N*-vinyl derivatives. β-Chloroethylaniline (cf. Nemirowsky, A., 1885, 741) is unstable; it "polymerises" to a chlorine-free solid substance of unknown constitution; its *hydrochloride*, m. p. 156—158°, is obtained by hydrolysing the above toluene-*p*-sulphonyl derivative with a mixture of acetic and hydrochloric acids. When part of the product is directly benzoylated (using a benzene solution of benzoyl chloride and an excess of sodium hydroxide), the chlorine atom is simultaneously removed and *benzo*-β-*hydroxyethylanilide*, m. p. 78°, is obtained. When β-chloroethylaniline hydrochloride is treated with sodium nitrite, it affords an oil which, by the action of alcoholic hydrogen chloride is converted into p-*nitroso*-β-*chloroethylaniline*, m. p. 90° (decomp. 120°), the *hydrochloride* of which has m. p. 182° (decomp.); when the intermediate oily nitrosoamine is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone, β-*chloroethyltetrahydrocarbazole*, m. p. 56—57°, is obtained, together with a *by-product*, m. p. 141°. 9-*Vinyltetrahydrocarbazole*, b. p. 210°/24 mm., is produced by the customary treatment with methyl-alcoholic potassium hydroxide. When this is treated with 50% sulphuric or alcoholic hydrochloric acid it is decomposed and a solid product is formed; this is due apparently to interaction of the acetaldehyde and tetrahydrocarbazole produced, because if a little hydrazine be added to the reaction mixture, tetrahydrocarbazole is obtained. 9-Vinyltetrahydrocarbazole cannot be prepared from 9-β-*hydroxyethyltetrahydrocarbazole*, m. p. 69—70°, b. p. 230—235°/14 mm., which is obtained when β-hydroxyethylphenylnitrosoamine is reduced, as above, in presence of *cyclo*hexanone. Carbazole and β-chloroethyl toluene-*p*-sulphonate afford 9-β-*chloroethylcarbazole*, m. p. 130—131°, from which 9-*vinylcarbazole*, m. p. 66°, is readily obtained. This also is decomposed by acids, when hydrazine is present, and carbazole is regenerated; if the hydrazine be absent, a complex solid *substance* is produced.

W. A. S.

Reduction Products of 1-Nitro- and 3-Nitro-carbazole. T. C. Whitner, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 2326—2329). —3-Nitro- and 1-nitro-carbazole, obtained by nitration of carb-

azole in acetic acid at 60° (cf. Ziersch, A., 1909, i, 961), on heating with alcoholic sodium or potassium hydroxide are reduced to *3-azoxycarbazole*, yellow, m. p. 208—209°, and *1-azoxycarbazole*, yellow, m. p. 183—185°, respectively, in yields of 70—80%. Reduction of the azoxycarbazoles in alcoholic solution with zinc dust gives an 80% yield of *3-azocarbazole*, red, m. p. 215°, and *1-azocarbazole*, reddish-brown, m. p. 196—197°, respectively. Reduction of 1-nitro-, 1-azoxy-, or 1-azo-carbazole with zinc dust in alcoholic potassium hydroxide yields 1-aminocarbazole, m. p. 226—228° (*acetyl* derivative, m. p. 170—171°). 3-Aminocarbazole, m. p. 254° (cf. Ruff and Stein, A., 1901, i, 619; Ullmann, A., 1898, i, 591) is similarly obtained from the corresponding 3-carbazole derivatives. R. B.

3-Hydroxyquinoline-4-carboxylic Acids. S. Berlingozzi and G. B. Capuano (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 91—94).—3-Hydroxy-2-methylquinoline-4-carboxylic acid (cf. this vol., i, 314) may be obtained by the condensation of isatoic acid with chloroacetone in presence of sodium hydroxide, and 3-hydroxy-2-phenylquinoline-4-carboxylic acid (*loc. cit.*) by the similar condensation of isatoic acid with ω-bromoacetophenone (cf. also A., 1923, i, 482).

3-Hydroxy-2-p-anisylquinoline-4-carboxylic acid, prepared similarly from isatoic acid and *p*-chloroacetylanisole, crystallises in lustrous, golden-yellow rosettes, m. p. about 190° (decomp.), and forms an intensely fluorescent alcoholic solution. When heated above its melting point, it loses carbon dioxide with formation of 3-hydroxy-2-*p*-anisylquinoline (cf. A., 1923, i, 483). The colours of various (precipitated) salts of the above acids are recorded. T. H. P.

Structure of the Protein Molecule. E. Abderhalden and E. Schwab (*Z. physiol. Chem.*, 1924, **139**, 68—75).—By condensation of *iso*butylpiperazine (this vol., i, 876) with α-bromo*iso*hexoyl bromide, *di-α-bromoisohexoylisobutylpiperazine*, m. p. 283° (decomp.) after previously sintering, has been obtained. This reacts with ammonia to form *dileucylisobutylpiperazine*, which, on reduction by the method previously employed (*loc. cit.*) yields a mixture of *iso*butylpiperazine and reduced dileucyl*iso*butylpiperazine (isolated as the *tetrahydrochloride*, $C_{20}H_{48}N_4Cl_4$). By similar methods of reduction, *β-amino-δ-methylpentan-α-ol* (*leucinol*), $CHMe_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH$, isolated as the *hydrochloride*, has been obtained from leucylglycine, and *2-methylpiperazine*, m. p. 245°, from glycyl-*d*-alanine anhydride. *Dichloroacetylmethylpiperazine* on treatment with ammonia gives *diglycylmethylpiperazine*. E. S.

Preparation of Compounds of Diketopiperazines with Amino-acids and Polypeptides. E. Abderhalden and E. Klarmann (*Z. physiol. Chem.*, 1924, **139**, 64—67).—When refluxed with chloroacetyl chloride for 2 hours at 60—70°, 2 : 5-dihydroxydihydropyrazine dibenzyl ether (Karrer, Gränacher, and Schlosser, this vol., i, 212) yields 1 : 4-di[chloroacetyl]-2 : 5-diketopiperazine

(A., 1923, i, 1025; this vol., i, 877), and not the expected *O*-dichloroacetyl derivative.

By heating glycine anhydride for 4 hours at 160° with thionyl chloride, a *substance*, $C_4H_2ON_2Cl_3$, m. p. 168—169° (uncorr.), is obtained. E. S.

Formation of Diketopiperazines from Polypeptides. E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **139**, 147—168).—On heating in a sealed tube at 150—160° for 6 hours with water, dilute hydrochloric acid, or dilute sulphuric acid, dipeptides give the corresponding anhydrides (diketopiperazines) in a yield which may vary from 20—90% of the theoretical. The only exception to this statement so far encountered is *dl*-valyl-*dl*-leucine, which gave no anhydride under these conditions. Prolonged boiling of the dipeptides in aqueous solution gave only traces of anhydrides. Small amounts of anhydrides have been obtained similarly from some tripeptides, but in no case where the tripeptide was composed of more than two different amino-acids. C. R. H.

Parabanic Acid. R. Andreasch (*Monatsh.*, 1924, **45**, 9—12).—Thiocarbamide and cyanogen do not form thioparabanic acid. Interaction of acetylthiocarbamide and chloroacetic acid gave thiohydantoin. Attempts to add cyanogen to acetylthiocarbamide, and to carbamide and its methyl and phenyl derivatives were unsuccessful. Ethylparabanic acid has m. p. 127—128°.

The product of reduction of dimethylparabanic acid or cholestrophan (A., 1882, 1054) is definitely proved to be 5-hydroxy-1 : 3-dimethylhydantoin (cf. Biltz and Heidrich, A., 1921, i, 817), since it is shown that for its reoxidation to cholestrophan, dichromate equivalent to two hydrogen atoms per mol. is required. F. M. H.

"Indigosol." A. Beil (*Z. angew. Chem.*, 1924, **37**, 745—746).—Leuco-indigotin is converted into an acid ester by treatment, in the presence of a tertiary base, with sulphur trioxide or substances which liberate it. The sodium salt of the ester, *Indigosol O*, is a nearly colourless powder, stable in the air and easily soluble in water, is unaffected by alkalis, and is decomposed by mineral acids only on prolonged boiling. Indigotin is regenerated by gentle oxidation (*e.g.*, with ferric chloride, or sodium nitrite, dichromate, or chlorates) in the presence of an acid. Indigosol has no affinity for vegetable fibres, but is substantive for wool, and possesses many practical advantages for the dyeing and printing of cotton and wool. [Cf. *B.*, 1924, 934.] W. T. K. B.

Indole Group. XI. Di-indylmethane. B. Oddo and G. Sanna (*Gazzetta*, 1924, **54**, 682—687).—An attempt to prepare an indole derivative corresponding with hexaphenylethane by treating magnesium indolyl (or 2-methylindolyl) bromide with carbon tetrachloride did not give the expected result, since, under the most varied conditions, this reaction yielded always the di-

substituted methane derivative which is obtained from magnesium indolyl bromide and chloroform (A., 1922, i, 313; 1923, i, 715). Apparently attachment of more than two indole nuclei to one and the same carbon atom is not possible, probably owing to the proclivity of such nuclei to pass into the coloured indolidenic form. The reaction of magnesium 2-methylindolyl bromide with carbon tetrachloride may result in the initial formation of either (1) the normal trisubstituted leuco-derivative, which undergoes subsequent decomposition into the disubstituted coloured base: $\left(NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\right)_2CCl\cdot C<\begin{matrix}C_6H_4\\CMe\end{matrix}>NH \rightarrow C_6H_4<\begin{matrix}CCl\\NH\end{matrix}>CMe +$ $NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CH{:}C<\begin{matrix}C_6H_4\\CMe\end{matrix}>N$, or (2) a dichloro compound, which then reacts with the excess of magnesyl derivative to form the same base: $\left(NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\right)_2CCl_2 + NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot MgBr =$ $MgBrCl + NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>CCl + NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CH{:}C<\begin{matrix}C_6H_4\\CMe\end{matrix}>N.$

T. H. P.

Isomeric Acylindazoles of K. von Auwers. J. MEISENHEIMER and A. DIEDRICH (*Ber.*, 1924, 57, [*B*], 1715—1723).—The general existence of 2-acylindazoles in isomeric labile and stable forms has been attributed by von Auwers and his co-workers (A., 1919, i, 455; 1920, i, 638, 640; 1922, i, 682, 684) to stereoisomerism conditioned by the presence of an asymmetric tervalent nitrogen atom. This conception is compatible with the tricyclic constitution of indazoles, but cannot be extended to the more recently adopted dicyclic constitution (cf. von Auwers, this vol., i, 878). The non-formation of stereoisomerides from 3-substituted indazoles suggests the possibility that one form of the "isomerides" is actually a 3-derivative, but this view is not supported by the experimental evidence now adduced. The only remaining alternative to the acceptance of the stereoisomeric formulation lies in the possibility that one form is a 1-compound. This conception has been rejected by von Auwers, since 1-acetylindazole, obtained from *o*-aminobenzaldoxime, is not identical with either of the "stereoisomeric 2-acetylindazoles." Re-examination of the former product renders very probable that it is not a derivative of indazole but is derived from the seven-membered ring, $C<\begin{matrix}C{-}C{:}N\\N{:}C{\cdot}O\end{matrix}$. The products described by von Auwers are therefore regarded as 1- and 2-acylindazoles.

3-*Benzoylindazole*, m. p. 188—189°, is prepared by the action of a considerable excess of magnesium phenyl bromide on 3-cyanoindazole in ethereal solution; the *acetyl* derivative, m. p. 121°, 2 : 4-*dinitrophenylhydrazone*, m. p. 277°, and the *oxime*, m. p. 175°, are described. 3-*Acetylindazole*, m. p. 182°, yields an *acetyl* derivative, m. p. 123°, an *oxime*, m. p. 222°, and a 2 : 4-*dinitrophenylhydrazone*, m. p. above 320°. The acyl compounds differ completely from von Auwers' "stereoisomeric" acetyl- and benzoyl-indazoles.

o-Aminobenzaldoxime is readily converted by glacial acetic acid and acetic anhydride into *o*-acetamidobenzaldoxime, which is transformed by concentrated sulphuric acid into "4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine" $C_6H_4<\begin{matrix}C(OH):N\\N=CMe\end{matrix}>O$ (von Auwers' 1-acetylindazole). The substance is oxidised by perbenzoic acid in alcoholic solution to *3-hydroxy-4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine*, $C_6H_4<\begin{matrix}C(OH):N\\N=CMe\end{matrix}>O$, m. p. 209°; attempts to establish the constitution of the compound by its production from the oxime of methyl acetylanthranilate were unsuccessful. *3-Acetoxy-4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine* has m.p. 117°. If von Auwers' conception is adopted the compound just mentioned must be identical with the diacetyl derivative of *o*-hydrazinobenzoic anhydride, m. p. 113—114°, and the oxidation product with *monoacetyl-o-hydrazinobenzoic anhydride*, m. p. 211°; this, however, is not the case. The oxidised product may be regarded as a cyclic ether of benzhydroxamic acid; it could not be synthesised from *o*-aminobenzhydroxamic acid since the latter is immediately converted by acetic anhydride into the *diacetyl* derivative, m. p. 128°, with which, after hydrolysis, the desired ring closure could not be effected. H. W.

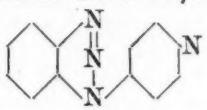
Constitution of Acylindazoles. K. von Auwers (*Ber.*, 1924, **57**, [*B*], 1723—1730).—As a result of the observations of Meisenheimer and Diedrich (preceding abstract) the constitution assigned previously to the "1-acylindazoles" is considered to have lost greatly in probability. The conception of these compounds as heptoxdiazines is not regarded as established, since the constitution of 3-hydroxy-7-methyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine has not been placed beyond doubt and proof has not been adduced that the oxidation takes place without rupture of the ring of the parent compound.

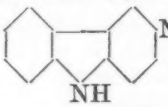
The "1-acylindazoles" are conveniently prepared by dissolving *o*-aminobenzaldoxime in the requisite acid and saturating the solution with dry hydrogen chloride at the atmospheric temperature or by treating a solution of the acylated oxime in glacial acetic acid in the same manner. "1-Acetylindazole" is converted by methyl iodide into an amorphous *methiodide*, $C_{10}H_{11}ON_2I$, decomp. above 90°, by bromine in glacial acetic acid into a very unstable *dibromide* and by the halogen in dilute hydrochloric acid solution into a *monobromo* derivative, m. p. 168—169°. 1-iso*Butyrylindazole* (or 7-iso*propyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*) has m. p. 108—108·5°; the *nitrate* and the additive *compound* with mercuric chloride dissolve sparingly in water. 1-iso*Valerylindazole* (7-iso*butyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*) has m. p. 85—86°, $d_4^{99·7}$ 1·0620, $n_\alpha^{99·4}$ 1·58638; the *nitrate* and the additive *compound* with mercuric chloride have been prepared. 1-*Benzoylindazole* (7-*phenyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*), m. p. 141° (the *nitrate* and the additive *compound* with mercuric chloride are described), is obtained from *o-benzamidobenzaldoxime*, m. p. 163—164°. *o*-Aminoacetophenoneoxime, propionic acid, propionic anhydride,

and hydrogen chloride yield 1-*propionyl*-3-*methylindazole* (3-*methyl*-7-*ethyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*), m. p. 138°, which gives a *nitrate* and an additive *compound* with mercuric chloride. 1-Formyl-3-phenylindazole (3-phenyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine), m. p. 167—168°, gives an additive *compound* with mercuric chloride. 1-*Benzoyl*-3-*phenylindazole* (3 : 7-*diphenyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*), m. p. 168—169°, and its additive *compound* with mercuric chloride are described.

Benzaldehyde and *o*-aminobenzaldoxime yield the *compound* $C_{14}H_{14}O_2N_2$, m. p. 135—136°, which gives a *monobenzoyl* derivative, m. p. 138—139°. The *benzoyl* derivative of *o*-nitrobenzaldoxime has m. p. 120—121°. H. W.

5-Carboline and some Derivatives. R. Robinson and S. Thornley (*J. Chem. Soc.*, 1924, **125**, 2169—2176).—N-γ-*Pyridyl*-*o*-*phenylenediamine*, m. p. 173·5°, obtained by heating 4-chloropyridine (b. p. 41°/13 mm.; 49°/18 mm.) with *o*-phenylenediamine at 98—140°/40 mm., forms a *hydrochloride*, and yields a *base*, probably γ-pyridylbenziminazole, m. p. 123°, when boiled in absolute formic acid. 1-γ-*Pyridylbenzotriazole* (I), m. p. 113·5°

(I.) 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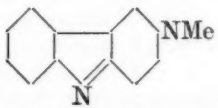
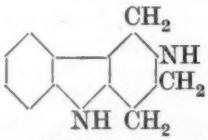
(III.) 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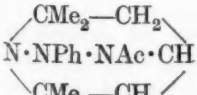
[*trihydrate*, m. p. 82°; *hydrochloride*, m. p. 262° (decomp.)], obtained from the above pyridyl-*o*-phenylenediamine by the action of nitrous acid, yields 5-*carboline* (II), m. p. 225°, when heated with excess of phosphoric acid (*d* 1·75). 5-Carboline distils unchanged at atmospheric pressure. The *hydrogen oxalate*, m. p. 226° (decomp.), and the *picrate* are described. The *methosulphate* when treated with hot concentrated potassium hydroxide yields 5-*methyl*-5-iso-*carboline* (III), m. p. 203—204°, subliming at 138° in a vacuum. This base is hygroscopic and its aqueous solution is strongly alkaline. The *methosulphate*, m. p. 210—211°, with potassium hydroxide gives a colourless precipitate. 5-Carboline is reduced by sodium and *n*-butyl alcohol to 3 : 4 : 5 : 6-*tetrahydro*-5-*carboline* (IV), m. p. 215·5°, a strong base; 5-*acetyl* derivative, m. p. after softening, 254·5°. *Acetyltriacetonaminephenylhydrazone*, m. p. 107°, could not be transformed into an indole derivative, and therefore possibly has the structure (V). When triacetonamine-methylphenylhydrazone is warmed with dilute sulphuric acid, 1 : 4 : 4 : 6 : 6-*pentamethyl*-3 : 4 : 5 : 6-*tetrahydro*-5-*carboline* is obtained. This (+1 MeOH) has m. p. 80—86° after softening at 78°. After being heated at 111°, the substance resolidifies, and has m. p. 92—93°. Crystallised from


(V.)

light petroleum, it has m. p. 180° after sintering at 160°, and partly melting and resolidifying at 170°. F. G. W.

Effect of Sulphur on the Colour of Triphenylmethane Dyes. H. S. Holt and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 2329—2333).—The auxochromic effect of the alkylthiol group in triphenylcarbinol derivatives observed by Brand and Stallmann (A., 1921, i, 664) has now been observed in a series of malachite-green derivatives containing the alkylthiol group in the ortho or para position in the third ring. The auxochromic effect is greatest when the sulphur occupies the para position, but diminishes with increasing mass of the alkyl group. The methylthiol group is a stronger auxochrome than methoxyl, and the shift is towards the blue.

p-Aminophenyl methyl sulphide, obtained by the methods previously described (Waldron and Reid, this vol., i, 95; Foster and Reid, this vol., i, 1243), when diazotised and treated with cuprous bromide and potassium bromide, yields p-*bromophenyl methyl sulphide*, m. p. 27°. p-*Bromophenyl* iso*propyl sulphide*, b. p. 120°/11 mm., d_{25}^{25} 1·2338; p-*bromophenyl* iso*amyl sulphide*, b. p. 140—143°/15 mm., d_{25}^{25} 1·1467; p-*bromophenyl benzyl sulphide*, m. p. 48°; p-*bromophenyl methyl sulphone*, yellow, m. p. 97·5°; o-*bromophenyl* iso*propyl sulphide*, b. p. 130—135°/11 mm., d_{25}^{25} 1·2804, and o-*bromophenyl phenyl sulphide*, b. p. 175—177°/12 mm., d_{25}^{25} 1·3733, were similarly prepared. With the exception of *p*-bromophenyl benzyl sulphide and methyl sulphone and *o*-bromophenyl phenyl sulphide, which do not react, these bromophenyl alkyl sulphides were convertible in presence of iodine into Grignard reagents; the latter when treated with Michler's ketone in benzene solution yielded the dyes $(NMe_2 \cdot C_6H_4)_2C(OH) \cdot C_6H_4 \cdot SR$ as orange solids turning green on exposure to air. R. B.

Constitution of Guinea-green B. H. Wales (*J. Amer. Chem. Soc.*, 1924, **46**, 2124—2128).—Guinea-green B is sodium hydrogen *s-pp'*-dibenzyldiethyldiaminotriphenylcarbinoldisulphonate. The free acid is brown and the disodium salt colourless, and the "organic material not dye" present in Guinea-green B is mainly the disodium salt. The free acid titrates very slowly with titanous chloride, and the higher results frequently obtained by very slow titration are due to the slow conversion of the disodium salt into the more readily reducible sodium hydrogen salt. The latter can be titrated in the presence of the disodium salt by titrating at 60—70° in the presence of sodium hydrogen tartrate. The titration can be checked by a spectrophotometric method, using a disodium phosphate–acetic acid buffer solution, p_H 6·0. R. B.

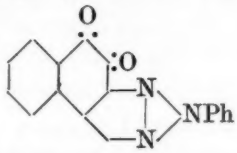
Reduction of certain Vat Dyes by means of Alkaline Sodium Hyposulphite. J. H. Yoe (*J. Physical Chem.*, 1924, **28**, 1211—1217).—The rate of reduction of ponsol-blue G (chloroanthraquinone-1 : 2 : 1′ : 2′-dihydroazine) by alkaline sodium hyposulphite at 40° is very great, the consequent peptisation, however, being less rapid, similar to ponsol-yellow G (A., 1923, i, 236).

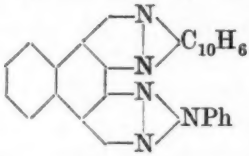
The reduced dye is in colloidal solution and is coagulated by salts. The amount of dye peptised was determined by the change in colour of the solution with time, and shows that the hyposulphite concentration has no effect above a certain value and that the optimum conditions are obtained with 0·25*N*-sodium hydroxide.

M. B. D.

o-Quinones derived from 2-Aryl-αβ-naphthatriazoles. G. CHARRIER (*Gazzetta*, 1924, **54**, 610—616).—Treatment of certain 2-aryl-αβ-naphthatriazoles with potassium dichromate and sulphuric acid under conditions which convert phenanthrene into phenanthraquinone results in the quantitative formation of the corresponding quinones. That the latter are ortho-quinones of the phenanthraquinone type is shown by their marked physical and chemical resemblance to phenanthraquinone and by their reaction with *o*-diamines to give the corresponding azines and with phenylhydrazine hydrochloride to form the hydroxyazo derivatives. It seems probable that anthracene bears the same relation to the ββ-naphthatriazoles that phenanthrene does to the αβ-naphthatriazoles.

2-*Phenyl*-αβ-*naphthatriazolequinone* (I), obtained by oxidation of

(I.) 

 (II.)

2-phenyl-αβ-naphthatriazole, forms orange-yellow needles, m. p. 207°, sublimes unchanged, and with hot alcoholic potassium hydroxide yields the brownish-green coloration characteristic for *o*-quinones. Its *benzeneazohydroxy* derivative,

$$NPh{:}N{\cdot}C_{10}H_4N_3Ph{\cdot}OH,$$

bright red needles, m. p. 232°, is obtained by the action of phenylhydrazine. The corresponding *naphthazine* (II), forms a microcrystalline, yellow powder, m. p. 262°, and yields deep red salts.

2-p-*Chlorophenyl*-αβ-*naphthatriazolequinone*, $C_{16}H_8O_2N_3Cl$, forms golden-yellow needles, m. p. 204°, its *benzeneazohydroxy* derivative, orange needles, m. p. 227°; the corresponding *naphthazine* is a yellow powder, m. p. 280°.

T. H. P.

Hydrolysis of Auramine. W. C. HOLMES and J. F. DARLING (*J. Amer. Chem. Soc.*, 1924, **46**, 2343—2348).—The hydrolysis of auramine in aqueous solution has been studied using a volumetric method based on the titration of the dye with a standard indigotin solution. The velocity of hydrolysis increases with the temperature and with the acidity of the solution, and, as in the hydrolysis of sucrose and of esters, the catalytic activity of the hydrogen ions is stimulated by the presence of other ions. The rate of hydrolysis is not influenced to a measurable extent by the relative purity of the dye samples used, and hydrolysis with dilute hydrochloric acid affords a convenient volumetric method for the determination

of auramine or auramine-G. At the end of the hydrolysis, the solution is made alkaline and the ammonia distilled over and titrated, the small amount of dye unhydrolysed by the acid being decomposed by the alkali into Michler's ketone and ammonia. Auramine-G is less readily hydrolysed than auramine. R. B.

Action of Azoimide on Azodicarboxylic Esters. R. Stollé and G. Adam (*Ber.*, 1924, **57**, [*B*], 1656—1659).—Azoimide and methyl azodicarboxylate in the presence of ethyl or amyl ether give 5-*methoxytetrazole*, $\begin{matrix}N\cdot NH\\ \|\\ N-N\end{matrix}\!\!>\!C\cdot OMe$, m. p. 159° (decomp.), and methyl iminodicarboxylate, $NH(CO_2Me)_2$, m. p. 134°. Under similar conditions, ethyl azodicarboxylate gives 5-hydroxytetrazole, 5-*ethoxytetrazole*, m. p. 98° (the *silver* salt is described), and ethyl iminodicarboxylate, m. p. 48°. The alkoxytetrazoles are readily hydrolysed by 20% hydrochloric acid to 5-hydroxytetrazole, m. p. 254° (decomp.). H. W.

Synthesis of Terephthal-green and Terephthal-brilliant-green from Cymene. M. T. Bogert and P. S. Nisson (*Proc. Nat. Acad. Sci.*, 1924, **10**, 421—426).—Terephthalyl chloride, prepared from cymene through methyl terephthalate (cf. Bogert and Harris, A., 1920, i, 65), interacts with dimethylaniline at 100° in presence of zinc chloride or other condensing agent, yielding the *dye* $C_6H_4\left[C\!<\!\begin{matrix}C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2Cl\end{matrix}\right]_2$, eventually isolated as zinc double salt. This compound is analogous to malachite-green and is termed by the authors "terephthal-green." The analogue of brilliant-green, termed "terephthal-brilliant-green" is obtained when diethylaniline is used. The two dyes both give yellower shades of green (on silk or wool) than their prototypes; they are more fugitive to light but faster than the latter to washing, milling, perspiration, and stoving, and are equally resistant to acid, alkali, or a bleaching solution. When terephthalyl chloride and dimethylaniline are brought together without a condensing agent, interaction takes place, not at 100°, but when the mixture is boiled; methyl chloride is evolved, and the *methylanilide*, $C_6H_4(CO\cdot NMePh)_2$, m. p. 212—213°, is formed (cf. the action of benzoyl chloride on dimethylaniline, Hess, A., 1885, 783). W. A. S.

Behaviour of Acetylene towards Nitrogen. L. Francesconi and A. Ciurlo (*Gazzetta*, 1924, **54**, 687—697).—Under the influence of the silent electric discharge, a mixture of acetylene and nitrogen yields a compound which contains nitrogen and has a fulvene structure, and may be termed *pernitrogenated azofulvene*. This compound forms reddish-yellow laminæ, has a strong aromatic odour, and decomposes violently, without melting, at above 210°. When heated in a closed tube with solid potassium hydroxide, a basic odour recalling that of nicotine is emitted. Like the similar substances described by Losanitsch (A., 1908, i, 866; ii, 32), the compound increases rapidly in weight in the air, giving a darker, opaque *peroxidised azofulvene* which decomposes violently at 230—

235° and effects active discharge of an electrometer. It absorbs chlorine, bromine, and iodine in considerable quantities and reacts with other substances. T. H. P.

Electrometric Studies on Azo and Hydrazo Compounds. E. Biilmann and J. H. Blom (*J. Chem. Soc.*, 1924, **125**, 1719—1731).—An investigation of the reduction potential of the system azo compound–hydrazo compound on the same lines as those with quinhydrone and alloxantin for subjects (cf. A., 1923, ii, 605; 1921, ii, 372).

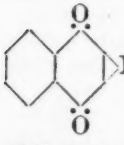
Two pairs of compounds were studied, *viz.*, 3 : 3′-diaminoazobenzene (termed azoaniline) and the corresponding hydrazo compound, and 3 : 3′-diamino-4 : 4′-dimethylazobenzene (termed azotoluidine) and the corresponding hydrazo compound. These were chosen because, being basic in character, they could be readily dissolved in acid to solutions of suitable concentration. At a temperature of 291° Abs. and a hydrogen pressure of 760 mm. the reduction potential for the azo–hydrazoaniline system (in 0·1*N*-hydrochloric acid) is 0·4137 volt, and for the azo–hydrazotoluidine system 0·3754 volt. The potential of the azo–hydrazo electrode, depending as it does on the proportion of azo to hydrazo compound, changes with time; this is evidently due to the conversion of the hydrazo compound into a benzidine or semidine derivative. From the observations made, the velocity constant of this conversion has been calculated for the two examples studied. W. A. S.

Preparation of Thio or Seleno Derivatives of Primary Aromatic Amines. Farbwerke vorm. Meister, Lucius, und Brüning (D.R.-P. 386615; from *Chem. Zentr.*, 1924, i, 2631).—Derivatives of the hypothetical thiohydroxylamine, $NH_2{\cdot}SH$, or dialkyldithiohydroxylamines, $RN(SR')_2$, are obtained by treating the condensation products of aromatic amines and aldehydesulphoxylates with hydrogen sulphide, mercaptans, etc., or hydrogen selenide, preferably in faintly acid solution:

$$R{\cdot}NH{\cdot}CH_2{\cdot}O{\cdot}SOH+R'{\cdot}SH=R{\cdot}NH{\cdot}SR'+CH_2O+S+H_2O.$$

The products separate as yellow precipitates; the following are described: *product* from hydrogen sulphide and *o*-toluidine *N*-methylenesulphoxylate, m. p. about 97°; the crystalline *product* from *p*-aminobenzoic acid and sodium formaldehydesulphoxylate, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}OSONa,2H_2O$, reacts with thioacetic acid to give S-*acetyl*-p-*thiohydroxylaminobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}SAc$, m. p. 153°. Anthranilidomethylenesulphoxylate and ethyl mercaptan afford p-*ethylthiohydroxylaminobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}SEt$, m. p. 97—99°. Aniline *N*-methylenesulphoxylate and thioacetic acid yield *SS*-diacetyldithiodihydroxyaniline, $NPh(SAc)_2$, m. p. 72°. Anthranilidomethylenesulphoxylate reacts with hydrogen selenide at 40—50° to give a *substance*, $C_{15}H_{14}O_6N_2SSe$, m. p. 40°, decomp. 80°. The condensation *product* of *o*-phenylenediamine and formaldehydesulphoxylate reacts with hydrogen selenide to give a *substance*, $C_{14}H_{19}O_7N_4S_3Se$, reddish crystals, m. p. 183—184°. F. A. M.

Derivatives of Azoimide. A. KORCZYŃSKI [with ST. NAMYSLOVKI] (*Bull. Soc. chim.*, 1924, [iv], **35**, 1186—1194).—The replacement of halogen atoms by azide groups when substituted quinones are treated with azoimide (Fries and Ochwat, A., 1923, i, 842) is a general reaction and mobile halogen atoms in compounds such as picryl chloride are replaced in the same way. With the unsubstituted naphthaquinones, azoimide reacts with the CH group ortho to the carbonyl yielding products, $C_{10}H_5O_2N$, which are analogous to the anthranils obtained by Schaarschmidt (A., 1916, i, 856) and by Gattermann (A., 1916, i, 857; 1921, i, 818). The diazido-α-naphthaquinone obtained by Fries and Ochwat (*loc. cit.*) could not be transformed into a dianthranil, and to account for the resistance of the benzene ring in the naphthalene molecule to the formation of a dianthranil, the annexed formula is suggested for the mono-anil. This finds some support in the behaviour of sulphuryl azide towards *p*-xylene (Curtius and Schmidt, A., 1922, i, 776). The azides are slightly stable, and although the azide group exercises an important influence on the colour of these compounds, this influence is irregular, and the azide group sometimes functions as a bathochrome and sometimes as hypsochrome, possibly in consequence of a change of structure in the group N_3, $\cdot N<\overset{N}{\underset{N}{\|}} \rightleftharpoons \cdot N{:}N{:}N$. The statement that azides on alkaline reduction yield hydrazo compounds could not be confirmed.



On treatment with one equivalent of sodium azide in glacial acetic acid at 100°, chloroanil is converted into 3 : 5 : 6-*trichloro*-2-*azido*-p-*benzoquinone*, dark orange needles, m. p. 147—149°, exploding slightly on rapid heating, whilst with two equivalents of azide in boiling alcoholic solution 3 : 6-dichloro-2 : 5-diazido-*p*-benzoquinone is obtained, a slight excess of sodium azide giving a small quantity of reddish-violet explosive *substance*, probably the triazidochloroquinone. Excess of sodium azide in alcoholic solution at 20° converts the trichloroazidoquinone into tetrazido-*p*-benzoquinone. Similarly, tetrabromo-*o*-benzoquinone in glacial acetic acid yields an explosive, black substance which is probably *tetra-azido*-o-*benzoquinone*. Tetrabromodiphenoquinone in alcoholic suspension yields tetra-azidodiphenoquinone, a black powder which explodes at 30° or by friction or shock. 1 : 4-Naphthaquinone in acetic acid with one equivalent of sodium azide yields 2 : 3-*imino*-1 : 4-*naphthaquinone*, reddish-brown laminæ, m. p. 203—204°, also crystallising with 1 mol. of acetic acid (lost at 110°). Similarly, 1 : 2-naphthaquinone yields 3 : 4-*imino*-1 : 2-*naphthaquinone*, brown laminæ, losing acetic acid of crystallisation at 110°, then decomp. 300°. 2-Aminofluorenone, obtained by reduction of 2-nitrofluorenone with sodium sulphide, on diazotisation and treatment of the diazonium chloride with sodium azide, gives 2-azidofluorenone, yellow laminæ, darkening at 115°, m. p. 117°, slightly explosive. On heating in an atmosphere of carbon dioxide, boiling in glacial acetic acid, or exposing to light, the azide is converted into a brown, amorphous *substance*, $C_{13}H_7ON$, not melting below 300°.

Similarly, aminoazobenzene is converted into p-*azidoazobenzene*, pale yellow needles, m. p. 91—93°, and toluylene-red, obtained by boiling *p*-nitrosodimethylaniline with *m*-tolylenediamine and treatment with ammonia to precipitate the colour but leave the hydro-base in solution, gives 3-*azido*-6-*dimethylamino*-2-*methylphenazine*, red needles, m. p. 171—172° (decomp.).

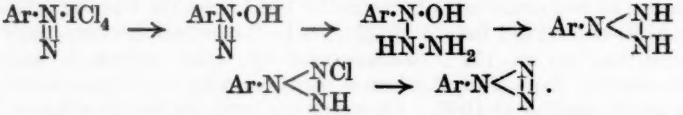
Picryl chloride in alcoholic solution reacts with aqueous sodium azide giving 2 : 4 : 6-trinitro-1-azidobenzene, m. p. 89—90° (decomp.), which darkens in colour on exposure to light and on boiling with acetic acid is converted into 4 : 6-*dinitro*-1 : 2-*dinitrosobenzene*, pale yellow needles, m. p. 172°, decomposed by light, which is also obtained directly from picryl chloride by the action of sodium azide in acetic acid solution at 100°. On warming with aniline in ethereal solution, picryl azide is converted into 2 : 4 : 6-trinitrodiphenylamine (Bamberger and Müller, A., 1900, i, 217). R. B.

Diazonium Tetrachloroiodides and Chloroplumbates. F. D. Chattaway, F. L. Garton, and G. D. Parkes (*J. Chem. Soc.*, 1924, **125**, 1980—1991).—Diazonium tetrachloroiodides, $Ar{\cdot}N_2(Cl_4I)$ (cf. Chattaway and Garton, this vol., i, 270), are obtained, in quantitative yield, when cooled solutions of diazonium chlorides are poured into cooled solutions of iodine trichloride in strong hydrochloric acid. They can be preserved indefinitely in sealed tubes or in an atmosphere of dry chlorine, and react generally in the same way as simple diazonium salts. With hydriodic acid, iodine is liberated quantitatively: $Ar{\cdot}N_2{\cdot}ICl_4+4HI=ArI+N_2+2I_2+4HCl$, this rendering iodometric analysis possible. When warmed with cuprous chloride or bromide in concentrated acid solution, or with potassium cyanocuprite, the diazonium tetrachloroiodides yield chloro, bromo, or cyano compounds, always accompanied by small quantities of the iodo derivative. The action of water yields phenols, with chlorophenols as by-products, whilst the action of alcohol causes the replacement of the diazo group chiefly by chlorine, and only to a lesser extent by hydrogen. The following *diazonium tetrachloroiodides*, yellow, crystalline powders, melting with decomposition at the temperatures quoted, are described: o-*toluene*-, 81·5°; p-*toluene*-, 95°; o-*chlorobenzene*-, 148°; p-*chlorobenzene*-, 111°; 2 : 4-*dichlorobenzene*-, 150°; 2 : 5-*dichlorobenzene*-, 141°; 2 : 4-*dibromobenzene*-, 120°; 2 : 4 : 6-*tribromobenzene*-, 135°; o-*nitrobenzene*, 125·5°; m-*nitrobenzene*-, 92°; and p-*nitrobenzene*-, 103°.

Diazonium chloroplumbates, $(Ar{\cdot}N_2)_2(PbCl_6)$, are obtained by the addition of solutions of diazonium salts to solutions of lead tetrachloride in strong hydrochloric acid. They form insoluble, yellow, crystalline solids, stable in the dry state, exploding at definite temperatures which vary only slightly according to the rate of heating. Their reactions are similar to those of the diazonium tetrachloroiodides, except for the absence of iodine. The following *diazonium chloroplumbates*, exploding at the temperatures stated, are described: o-*toluene*-, 78—80°; 2 : 4-*dichlorobenzene*-, 183—184°; p-*bromobenzene*-, 139—141°; 2 : 4-*dibromobenzene*-, 117—118°;

2 : 4 : 6-*tribromobenzene-*, 114—116°; o-*nitrobenzene-*, 120—122°. The following diazonium chloroplumbates previously described (Sakellarios, this vol., i, 220) explode at the following temperatures: benzene-, 80—81°; *p*-chlorobenzene-, 145—150°; *p*-toluene-, 72—75°; *m*-nitrobenzene-, 161—163°; and *p*-nitrobenzene-, 132—133°.

When diazonium tetrachloroiodides or chloroplumbates are added to concentrated aqueous ammonia, azoimides are obtained in good yields, probably according to the scheme:

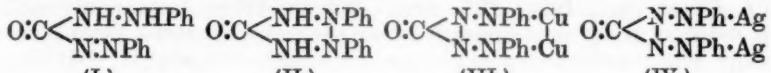


2 : 5-*Dichlorophenylazoimide*, pale yellow crystals, m. p. 30°, and o-*tolyl azoimide*, pale yellow oil, b. p. 70°/20 mm., are described.

1-(2 : 4-*Dichlorophenyl*)-1 : 2 : 3-*triazole*, obtained by the action of 2 : 4-dichlorophenylazoimide on acetylene in acetone solution at 100° under pressure (cf. Dimroth, A., 1910, i, 645), has m. p. 80°. 1-(2 : 5-*Dichlorophenyl*)-1 : 2 : 3-*triazole*, m. p. 78°; 1-(2 : 4-*dibromophenyl*)-1 : 2 : 3-*triazole*; 1-o-*tolyl*-1 : 2 : 3-*triazole*, yellow oil; and 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-1 : 2 : 3-*triazole*, pale yellow needles, m. p. 326° (decomp.), were prepared. o-Tolyl azoimide reacts with ethyl acetoacetate in presence of sodium ethoxide to form 1-o-*tolyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, m. p. 138° (decomp.), whilst the halogen substituted phenyl azoimides and diphenyl-4 : 4′-bisazoimide yield similarly the corresponding ethyl esters as primary products. *Ethyl* 1-(2 : 4-*dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, m. p. 270° (decomp.), yields on hydrolysis the free *acid*, m. p. 169·5° (decomp.); 1-(2 : 5-*dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* has m. p. 158°; *ethyl* 1-(2 : 4-*dibromophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, m. p. 302° (decomp.), yields the free *acid*, m. p. 173°; 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* has m. p. 245° (decomp.). The following 1 : 2 : 3-*triazoles* were prepared by heating the corresponding 4-carboxylic acids above their melting points: 1-(2 : 4-*dichlorophenyl*)-5-*methyl*-, m. p. 69°; 1-(2 : 5-*dichlorophenyl*)-5-*methyl*-, m. p. 51°; 1-(2 : 4-*dibromophenyl*)-5-*methyl*-, m. p. 87°; and 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 227°. Phenyl-1 : 2 : 3-triazoles unsubstituted in the triazole ring have strong, mushroom-like odours, whilst the corresponding 5-methyl derivatives are odourless. F. G. W.

Relationship between Atomic Grouping and Specific Affinity. II. Diphenylcarbazone, its Salts, and those of the supposed Diphenylcarbodiazone. F. Feigl and A. F. Lederer (*Monatsh.*, 1924, **45**, 63—68).—"Diphenylcarbodiazone" is regarded as a second form of diphenylcarbazone, and the structure of the isomerides and their salts is discussed. Certain discrepancies and anomalies are pointed out and theories of the constitution of the metallic salts of diphenylcarbazone and diphenylcarbodiazone are criticised (Cazeneuve, A., 1900, i, 465; 1901, i, 297). From

diphenylcarbazone (I) salts are derived by replacing the hydrogen atom of the anilino group by univalent metal. Cazeneuve's



(I.) (II.) (III.) (IV.)

directions for preparing diphenylcarbodiazone, m. p. below 100°, led to a product, m. p. 164° with explosion, which is considered to be a cyclic diphenylcarbazone (II). III represents a salt with a bivalent metal, and IV the likewise unstable silver salt.

F. M. H.

Organic Compounds of Arsenic. I. Carboxylated Aromatic Arsinic Acids and Arseno Compounds. E. MASCHMANN (*Ber.*, 1924, **57**, [*B*], 1759—1766).—*5-Amino-o-tolylarsinic acid*, m. p. 235—236° (decomp.) after darkening at 200°, is prepared by reducing 5-nitro-*o*-tolylarsinic acid with ferrous sulphate and sodium hydroxide at 80°. *5-Nitro-o-carboxyphenylarsinic acid*, m. p. 264—265° (decomp.) after darkening at 210°, obtained by the oxidation of 5-nitro-*o*-tolylarsinic acid by potassium permanganate, is reduced by sodium amalgam and methyl alcohol to *5-amino-o-carboxyphenylarsinic acid*, m. p. 219—220° (decomp.), which is converted by nitrous acid into *5-hydroxy-o-carboxyphenylarsinic acid*, decomp. indefinite. 5-Amino-*o*-tolylarsinic acid is diazotised and the diazonium solution is treated with cuprous cyanide; the nitrile thus obtained is hydrolysed by potassium hydroxide to *5-carboxy-o-tolylarsinic acid* which remains unchanged below 300°. The compound is oxidised by potassium permanganate in alkaline solution to *2 : 5-dicarboxyphenylarsinic acid*, decomp. indefinite. 5-Carboxy-*o*-tolylarsinic acid is converted by sulphuric acid and nitric acid (*d* 1·4) at 0—10° into *3-nitro-5-carboxy-o-tolylarsinic acid* which is unchanged below 300°; it is reduced by ferrous sulphate and sodium hydroxide to *3-amino-5-carboxy-o-tolylarsinic acid*. 2-Nitro-*p*-toluidine is transformed by diazotisation and treatment of the diazonium solution with sodium arsenite into *2-nitro-p-tolylarsinic acid*, m. p. 241—242° (decomp.), which is oxidised by potassium permanganate to *2-nitro-4-carboxyphenylarsinic acid*, m. p. 226—227° (decomp.), from which *2-amino-4-carboxyphenylarsinic acid*, decomp. 225—226° (the *acetyl* derivative is described), and *2-hydroxy-4-carboxyphenylarsinic acid*, decomp. indefinite, are obtained in the usual manner. 2-Nitro-*p*-tolylarsinic acid is reduced by sodium amalgam and methyl alcohol to *2-amino-p-tolylarsinic acid*, decomp. 185°. 5-Nitro-2-carboxyphenylarsinic acid is reduced by hypophosphorous acid and potassium iodide to *5 : 5′-diamino-2 : 2′-dicarboxyarsenobenzene*; *5 : 5′-dihydroxy-2 : 2′-dicarboxyarsenobenzene* and *3 : 3′-diamino-5 : 5′-dicarboxy-2′ : 2′-dimethylarsenobenzene* are prepared in a similar manner. *4 : 4′-Dicarboxy-2 : 2′-diaminoarsenobenzene* (the *hydrochloride* is described) is obtained by the action of stannous chloride and potassium iodide on 2-nitro-4-carboxyphenylarsinic acid.

H. W.

Organic Compounds of Arsenic. I. Derivatives of o-Benzarsinic Acid. J. A. AESCHLIMANN and N. P. MCCLELAND (*J. Chem. Soc.*, 1924, **125**, 2025—2035).—When benzarsinic acid is reduced in aqueous solution by sulphur dioxide and a little hydriodic acid, the *hydrated* o-*benzarsenious oxide*, $CO_2H{\cdot}C_6H_4{\cdot}As(OH)_2$, is obtained, which melts at 89° and resolidifies at 140° with formation of the anhydride, $\left[C_6H_4<\begin{matrix}CO\\As\end{matrix}>O\right]_2O$, m. p. 231° after sintering at 225°. Anhydrous o-*benzarsenious oxide* is obtained by crystallising the hydrated compound from ether or benzene. It yields o-*benzarsenious chloride* when treated with hydrogen chloride in benzene or chloroform, and this, on distillation in a vacuum, affords o-*carboxyphenylchloroarsinous anhydride*,

$$C_6H_4<\begin{matrix}CO\\AsCl\end{matrix}>O,$$

m. p. 145°, b. p. about 220°/15 mm., which is also obtained by distilling the product of the action of phosphorus trichloride on o-benzarsinic acid in chloroform. *Benzophenone*-o-*dichloroarsine*, $Bz{\cdot}C_6H_4{\cdot}AsCl_2$, m. p. 107—108°, was obtained from dichloro-o-arsinobenzoyl chloride (cf. Lewis and Cheetham, A., 1923, i, 407) and benzene using aluminium chloride in carbon disulphide. *Benzophenone*-o-*arsinic acid*, m. p. 215—219°, and *benzophenone*-o-*arsenious oxide*, m. p. 105—200° (incomplete), were obtained from the dichloroarsine by treatment with alkali and hydrogen peroxide, and alkali alone, respectively. By treating benzophenone-o-dichloroarsine with sodium hydroxide and methyl iodide, converting the resulting iodoarsine (m. p. 110—114°) into the oxide by means of alcoholic potassium hydroxide, and treating this with hydrogen chloride in benzene, *benzophenone*-o-*methylchloroarsine*, m. p. 88°, was obtained. Attempts to eliminate hydrogen chloride from this compound, by the action of aluminium chloride, failed. *Benzophenone*-o-*methylarsinic acid*, m. p. 186°, could not be dehydrated to form a ring compound.

o-*Carboxydiphenylarsinic anhydride* (I), m. p. not below 300°, was prepared by condensing benzenediazonium chloride with sodium benzarsinite. It is not affected by sulphuric acid at 100°. o-*Carboxydiphenylarsinous anhydride* (II), m. p. 133°, was obtained by reducing the above arsinic acid, and is also produced by the

$$C_6H_4<\begin{matrix}CO\\As\end{matrix}>O \quad C_6H_4<\begin{matrix}CO\\As\end{matrix}>O \quad C_6H_4<\begin{matrix}CO\\As\end{matrix}>O \quad C_6H_4<\begin{matrix}CO\\AsO\end{matrix}>O$$
$$\text{(I.) } PhO{\cdot}OH \qquad \text{(II.) } Ph \qquad \text{(III.) } Me \qquad \text{(IV.) } C_6H_4{\cdot}CO_2H$$

distillation, in a vacuum, of o-*carboxydiphenylchloroarsine*, m. p. 163°, prepared by condensing an alkaline solution of phenyldichloroarsine with diazotised anthranilic acid, reducing the product with sulphur dioxide, and treating the resulting acid with hydrogen chloride in benzene. On crystallising this compound (m. p. 163°) from benzene, a *product*, m. p. 125°, was obtained. The *acid chloride* of o-carboxydiphenylchloroarsine distils unchanged in a vacuum and partly crystallises. Treated with aluminium chloride,

it yields benzophenone-*o*-dichloroarsine. *o-Carboxyphenylmethylarsinous anhydride* (III), m. p. 106°, b. p. 220°/15 mm., obtained by the action of methyl iodide and sodium hydroxide on benzarsenious oxide, yields *o-carboxyphenylmethylarsinic acid*, m. p. 310°, on oxidation, and this, on reduction and treatment of the reduction product with hydrogen chloride in benzene, affords *o-carboxyphenylmethylchloroarsine*, m. p. 141°, which loses hydrogen chloride on distillation in a vacuum. *oo'-Dicarboxydiphenylarsinic anhydride* (IV), m. p. 255°, obtained by condensing benzarsenious oxide with diazotised anthranilic acid, yields *oo'-dicarboxydiphenylarsinous anhydride*, m. p. 251—255°, on reduction, and this, on treatment with hydrogen chloride in methyl alcohol, affords *oo'-dicarbomethoxydiphenylchloroarsine*, m. p. 184°. F. G. W.

Residual Affinity and Co-ordination. XX. Chromic and Cobaltic Lakes of Mordant Azo-dyes. G. T. Morgan and J. D. M. Smith (*J. Chem. Soc.*, 1924, **125**, 1731—1739).—Eriochrome-red B (4-sulpho-β-naphthol-1 : 4′-azo-1′-phenyl-3′-methyl-5′-pyrazolone) contains one "chelate" group: it yields, with chromic fluoride, a *chromic* lake, and, with roseocobaltic chloride, first a *cobaltic* lake, then the *mono-* and *di-roseocobaltic* salts of the latter. Similarly, Palatine-chrome-black 6B (β-naphthol-1 : 1′-azo-β-naphthol-4-sulphonic acid) yields *chromic* and *cobaltic* lakes and the *diroseocobaltic* salt of the latter. Diamond-black PV (1 : 5-dihydroxynaphthalene-2 : 2′-azophenol-4′-sulphonic acid) yields a *chromic* lake, but with roseocobaltic chloride affords only the lake of the oxidised dye (8-hydroxy-α-naphthaquinone-7 : 2′-azophenol-4′-sulphonic acid) and its *mono-* and *di-roseocobaltic* salts. Metachrome-brown B (4 : 6-dinitrophenol-2-azo-*m*-toluylenediamine) gives a *cobaltic* lake. *o*-Carboxybenzeneazo-β-naphthol affords a *diroseocobaltic* salt of the cobaltic lake, and from *m*-acetylbenzeneazo-β-naphthol-6-sulphonic acid only the *triammonium monoroseocobaltic* salt is obtained. Constitutional formulæ for these compounds are discussed (cf. T., 1922, **121**, 2857, etc.).
W. A. S.

Residual Affinity and Co-ordination. XXI. Boron β-Diketone Difluorides. G. T. Morgan and R. B. Tunstall (*J. Chem. Soc.*, 1924, **125**, 1963—1967).—Boron trifluoride reacts with β-diketones, but unlike the trichloride yields no boronium salt, but a difluoride, in which there is no ionisable fluorine atom. Thus, with acetylacetone, reaction takes place and heat is evolved, *boron acetylacetone difluoride*, $CH\langle^{CMe{\cdot}O}_{CMe{:}O}\rangle BF_2$, m. p. 43°, is obtained. *Boron benzoylacetone difluoride*, m. p. 155°, and *boron dibenzoylmethane difluoride*, m. p. 191°, were prepared in a similar way. Analytical methods are described. W. A. S.

Residual Affinity and Co-ordination. XXII. Optically Active Salicylatocobalt Diethylenediammines. G. T. Morgan and J. D. M. Smith (*J. Chem. Soc.*, 1924, **125**, 1996—2004).—*Salicylatodiethylenediamminecobaltic chloride dihydrate*, $YCl(H_2O)_2$,

where Y is the complex $en_2Co<^{O\text{—}}_{O\cdot CO}>C_6H_4$, was obtained as purplish-red plates by treating *trans*-dichlorodiethylenediamminecobaltic chloride with silver oxide and adding salicylic acid (1 mol.) to the filtrate. As a by-product, *disalicylatodiethylenediamminecobaltic salicylate*, $[en_2Co(C_7H_5O_3)_2]C_7H_5O_3$, was obtained as pale violet-pink needles. The *carbonato dihydrate*, $Y_2CO_3(H_2O)_2$, violet-red plates, was obtained from the above chloride by the action of silver carbonate, and was converted by treatment with *d*- and *l*-camphorsulphonic acids, respectively, into l-*complex*-d-*camphorsulphonate*, $YC_{10}H_{15}O_4S(H_2O)_2$, bright red plates, $[\alpha]_{Li_{5700}}$ −41·3°, $[M]_{Li}$ for the complex ion −290·4°, and d-*complex*-l-*camphorsulphonate*, $[\alpha]_{Li}$ +33°, $[M]_{Li}$ for the complex ion +242·1°. From these optically active salts the following were obtained by double decomposition: d- and l-*chloromercurate hydrates*, $[YH_2O]HgCl_3$, $[M]_{Li}$ +288° and −294·4°, respectively; and d- and l-*bromomercurate hydrates*, $[YH_2O]HgBr_3$, $[M]_{Li}$ ±294°. The racemic halomercurates form purplish-red plates of paler tint than the active isomerides, and are much less soluble in water. The active salts remain active if crystallised from boiling water, or left in solution for six weeks. The following racemoid salts are also described: *iodomercurate hydrate*, YH_2O,HgI_3, dark purple-red, flattened needles; *nitrate trihydrate*, $YNO_3(H_2O)_3$, dark red, deliquescent needles; *hydrogen dichloride trihydrate*, $YHCl_2(H_2O)_3$, scarlet, plates; *hydrogen dinitrate*, $YH(NO_3)_2$, dark red plates; and *hydrogen carbonate*, $YHCO_3$, bright red, diamond-shaped and six-sided plates. The retention of only one mol. of water or one hydrion in the complex ion is ascribed to the unique affinity of the one carbonyl oxygen of the complex. An analogous explanation is suggested for the formation of oxonium salts. F. G. W.

Relation of Chemical Structure to Rate of Hydrolysis of Peptides. I. Synthesis, Physical Constants, and Rates of Hydrolysis of Methylated Peptides. P. A. Levene, H. S. Simms, and M. H. Pfaltz (*J. Biol. Chem.*, 1924, **61**, 445—464).—Glycylsarcosine, sarcosylglycine, and sarcosylsarcosine have been synthesised, their dissociation constants, isoelectric points, and relative rates of hydrolysis determined and compared with corresponding values for glycylglycine. (In the following, k_a represents the acidic dissociation constant, k_b that of the amino group.) *Glycylsarcosine*, from chloroacetylsarcosine and ammonium hydroxide, has m. p. 200—201°, k_a $1{\cdot}48\times10^{-3}$, k_b $0{\cdot}576\times10^{-5}$, isoelectric point p_H 5·68. *Sarcosylglycine*, from chloroacetylglycine and methylamine, has m. p. 195—197°, k_a $0{\cdot}794\times10^{-3}$, k_b $0{\cdot}537\times10^{-5}$, isoelectric point p_H 5·80. *Sarcosylsarcosine* has m. p. 180—185°, k_a $1{\cdot}38\times10^{-3}$, k_b $2{\cdot}09\times10^{-5}$, isoelectric point p_H 5·98. Glycylglycine has k_a $0{\cdot}759\times10^{-3}$, k_b $0{\cdot}195\times10^{-5}$, isoelectric point p_H 5·59. The hydrolyses were conducted at 100° with 1 mol. equivalent of acid; under these conditions all except sarcosylsarcosine followed the normal course of a bimolecular reaction; hydrolysis experiments with smaller quantities of acid indicate that anhydride formation

is probably the explanation of the anomalous behaviour of sarcosylsarcosine. C. R. H.

Anhydride Structure of Silk Fibroin. E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1924, **139**, 169—180).—Among the products of the reduction, by sodium and alcohol, of silk peptone (obtained by hydrolysing silk fibroin with 70% sulphuric acid at incubator temperature) there have been isolated methylpiperazine, 3-*methyl*-6-*hydroxymethylpiperazine* (as *dihydrochloride*) and a compound which appears to be the *tetrahydrochloride* of the piperazine corresponding to an anhydride of the glycylalanylglycyltyrosine previously obtained by Fischer and Abderhalden (A., 1907, i, 737) from silk fibroin. For comparison with this compound the authors prepared 2 : 6-*di*-p-*hydroxyphenylmethylpiperazine* by the reduction of tyrosine anhydride; this piperazine gives a *hydrochloride*, m. p. 265°, and does not give Millon's reaction. By the hydrolysis of silk fibroin with cold 70% sulphuric acid, alanylserine anhydride and an *anhydride* (alanine, tyrosine, glycine, 1 : 1 : 2 mols., less water, 4 mols.) were obtained. The latter gave a negative ninhydrin reaction and a positive picrate test, whereas a similar compound obtained previously (*loc. cit.*) had these properties reversed. It is from the alanylserine anhydride, presumably, that the methylhydroxymethylpiperazine is formed. C. R. H.

Anhydride Structure of Proteins. E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **139**, 181—204).—The fact that Jaffé's reaction for creatinine (A., 1886, 1056) is given by diketopiperazines in general has been confirmed by tests carried out on the anhydrides of numerous amino-acids and dipeptides; in all cases the reaction was positive in the case of the anhydride and negative with the original amino-acid or peptide. Similar results were obtained with the reaction of von Bittó using *m*-dinitrobenzene and *m*-phenylenediamine. These two reactions have been utilised to investigate the question of the occurrence in proteins of preformed diketopiperazines; in many proteins and in the peptones derived therefrom, it was possible to demonstrate the presence of such compounds. The significance of this result in relation to the theory of the constitution of proteins is fully discussed. Included in the paper is a severe criticism of the work of Ssadikov and Zelinsky (this vol., i, 1122). C. R. H.

Origin of the Humin formed during the Acid Hydrolysis of Proteins. R. A. GORTNER (*Z. physiol. Chem.*, 1924, **139**, 95—96).—Polemical (cf. Edlbacher, this vol., i, 891). E. S.

Dakin's Method Applied to Edestin. T. B. OSBORNE, C. S. LEAVENWORTH, and L. S. NOLAN (*J. Biol. Chem.*, 1924, **61**, 309—313).—Dakin's butyl alcohol method of extraction (A., 1919, i, 150) has been modified by dropping the concentrated solution of amino-acids into 7 volumes of butyl alcohol, which is rapidly stirred at the ordinary temperature. The products of hydrolysis of edestin were investigated by this method; no evidence could be obtained of the presence of β-hydroxyglutamic acid, which, in

view of the fact that edestin may serve as the sole source of protein in a satisfactory diet for young rats, indicates that this amino-acid is not essential for growth. Part of the dry residue of the butyl alcohol extract was soluble in ethyl alcohol and appeared to consist of diketopiperazines. C. R. H.

Basic Amino-acids Yielded by Casein. C. S. LEAVENWORTH (*J. Biol. Chem.*, 1924, **61**, 315—316).—The nitrogen, other than that of lysine, contained in the substances which can be precipitated by phosphotungstic acid from the products of hydrolysis of casein, amounts to 1·1% of the total nitrogen of the casein; it is therefore improbable that casein contains any hitherto unidentified basic amino-acid. C. R. H.

Correlation between the Spectra of various Hæmoglobins and their Relative Affinities for Oxygen and Carbon Monoxide. M. L. ANSON, J. BARCROFT, A. E. MIRKSY, and S. OINUMA (*Proc. Roy. Soc.*, 1924, **B**, **97**, 61—83).—The relation $\log K = 0{\cdot}05 \times$ span, in which K is the equilibrium constant of the equation $CO + HbO_2 \rightleftarrows CO\text{–}Hb + O_2$ and the "span" is the difference, in Ångström units, between the positions of maximum intensity of the α-oxyhæmoglobin and carbon monoxide–hæmoglobin spectral bands, has been found to hold for the hæmoglobins from a number of mammals. The span varies from 43 to 56 units in different species and also in individuals of the same species; these variations appear to be due to the specificity of the globin portion of the molecule. The similar relation $\log 1/C_{T_1} - \log 1/C_{T_2} = 0{\cdot}049\ (A_{T_1} - A_{T_2})$ exists between the shift in the absorption bands and change in affinity of hæmoglobin for oxygen during change in temperature; C_{T_1} and C_{T_2} represent, at temperatures T_1 and T_2, respectively, the concentration of oxygen in solution when the hæmoglobin is half-saturated, and A_{T_1} and A_{T_2} the corresponding positions of maximum intensity of the α-bands. E. S.

Hexagonal Crystals of Horse Hæmoglobin. E. MÖLLENHOFF (*Z. Biol.*, 1924, **82**, 153—154).—Hexagonal crystals can be obtained without putrefaction taking place. The action which takes place during putrefaction is considered to be one of reduction. O. O.

The Carbohydrate Group of Thymus-nucleic Acid. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1924, **139**, 205—211; cf. this vol., i, 439).—The "glucal" reactions of Feulgen (A., 1914, i, 1098; 1918, i, 85; this vol., i, 1132) for thymus-nucleic acid are due to the elimination from the carbohydrate part of the molecule of 2-hydroxymethylfurfuraldehyde; these reactions are not given by dextrose itself, but are obtained (especially the green pine-shaving reaction) with more or less intensity in the cases of some di- and poly-saccharides and glucosides. The variations in the reactions are apparently due to differences in the linking of the carbohydrate portion to the rest of the molecule. C. R. H.

Biochemistry.

Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. IV—VI. A. V. HILL, C. H. N. LONG, and H. LUPTON (*Proc. Roy. Soc.*, 1924, **B**, **97**, 84—138).—IV. *Methods of studying the respiratory exchanges in man, during rapid alterations produced by muscular exercise, and while breathing various gas mixtures.*—The Douglas bag is considered more satisfactory than the closed gas chamber. The technique of the method is discussed with special reference to gaseous mixtures containing a high proportion of oxygen. Where the mixtures contain more than 50% of oxygen serious errors are liable to occur.

V. *The recovery process after exercise in man.*—After moderate short-lived exercise recovery is rapid and practically complete in a few minutes. This is due to the oxidative removal of lactic acid in the muscles where it was formed. After severe or prolonged exercise, the same initial rapid phase occurs, but this is followed by a protracted process, which represents the oxidative removal of lactic acid which has had time (owing to an inadequate oxygen supply) to diffuse from the muscles. These facts enable a distinction to be made between "moderate" exertion, which is followed by the initial phase only, and "severe" exertion, which is followed by both phases. During the early stages of recovery after severe exercise there is an elimination of carbon dioxide and a high respiratory quotient; during the later stages, a retention of carbon dioxide and a low respiratory quotient. The carbon dioxide so retained was used as a measure of lactic acid removed, and the oxygen used in recovery as a measure of the energy used in the removal of the acid. From these two quantities the "efficiency" of recovery in man has been calculated and found to agree with the value obtained for isolated frogs' muscle and also with that found by the amount of the lactic acid removed during any recovery interval compared with the recovery oxygen used in that interval. The time course of the recovery process while breathing oxygen-enriched air is not appreciably different from that while breathing atmospheric air, and the main process of recovery is practically unaffected by the higher oxygen pressures.

VI. *The oxygen debt at the end of exercise.*—Only about 5% of the oxygen debt is due to the extra circulatory and respiratory effort associated with recovery. It is considered that the remainder is utilised in restoring lactic acid to its precursor. The breathing of oxygen mixtures allows a considerable increase in the maximum oxygen debt. (Cf. this vol., i, 1128.) O. O.

Content of Sodium Chloride in the Blood of certain Marine Invertebrates. M. DUVAL (*Compt. rend.*, 1924, **179**, 706—708).—The blood of various marine invertebrates, especially of the crustaceans, contains appreciably less sodium chloride than the

sea-water in which they are found. Equality between the osmotic pressures of the blood and of the water is effected by the other components of the blood. The blood of *Siponculus nudus*, however, contains exactly the same proportion of sodium chloride as sea-water. T. H. P.

Changes in Blood Electrolytes in Ether Acidosis. J. H. Austin, G. E. Cullen, H. C. Gram, and H. W. Robinson (*J. Biol. Chem.*, 1924, **61**, 829—840).—In the acidosis following ether anæsthesia there is, in the blood, a rise in the concentration of chloride ion, a fall in that of hydrogen carbonate, and a slight fall in that of the total base. These observations are, in themselves, insufficient to account for the increase in hydrogen-ion concentration which is simultaneously observed, and necessitate the hypothesis that the increased acidity is brought about by the presence of other unidentified anions. The authors suggest the liberation of lactic acid in the tissues as a possible cause of the phenomenon. (In this connexion, cf. Ronzoni, Koechig, and Eaton, this vol., i, 1258.) C. R. H.

Experimental Alterations in the Calcium Content of Human Serum and Urine. C. P. Stewart and J. B. S. Haldane (*Biochem. J.*, 1924, **18**, 855—857).—The calcium content of human serum can be raised by 10 to 20% by ingestion of calcium and ammonium chlorides, by breathing 6 to 7% carbon dioxide, or by forced breathing. It can be lowered by 10 to 20% by ingestion of sodium hydrogen carbonate. The urinary calcium output is increased by ingestion of ammonium chloride and is little affected by sodium hydrogen carbonate. S. S. Z.

Changes in the Phosphorus Partition in Human Blood during Ammonium Chloride Acidosis. H. D. Kay (*Biochem. J.*, 1924, **18**, 1133—1138).—There is a rise in inorganic phosphorus during ammonium chloride acidosis. The "lecithin" or lipin phosphorus changes in a similar way in this condition. The organic acid-soluble phosphorus (*i.e.*, the organic fraction after precipitating the blood with trichloroacetic acid) shows an immediate fall at the outset followed by a slow return to normal after several days. This change takes place in the portion of the fraction which is resistant to hydrolysis by the bone enzyme. The significance of these changes is discussed. S. S. Z.

Chemical Changes in the Blood during Fasting and subsequent Re-feeding. S. Morgulis and A. C. Edwards (*Amer. J. Physiol.*, 1924, **68**, 477—498).—During prolonged fasting, the non-protein and urea nitrogen of the blood of dogs usually increases, then remains constant, and finally increases again; the amino-acid nitrogen remains constant or suffers at first a slight temporary diminution; the uric acid of the blood increases progressively; the creatinine remains constant, but the creatine first diminishes and then rapidly rises. The sugar and chlorides, which diminish at first, increase again during the later stages. When the animals are

once again fed, very extensive changes occur in the composition of the blood, which eventually reaches a normal condition.

A. A. E.

Chemical Changes in Blood of Dogs after Thyro-parathyroidectomy. I. GREENWALD (*J. Biol. Chem.*, 1924, **61**, 649—657).—After removal of the thyroids and parathyroids of dogs there was found, during the resulting tetany, no change in the titratable alkali, sugar, or nucleotide nitrogen of the blood, a decrease in the calcium, and a slight increase in the acid-soluble phosphorus; in view of the marked decrease in the excretion of phosphates which follows parathyroidectomy, it appears that, in this condition, phosphorus must be deposited in the tissues.

C. R. H.

Amino-acid Content of the Blood and its Significance as a Test of Liver Function. M. VON FALKENHAUSEN (*Arch. exp. Path. Pharm.*, 1924, **103**, 322—328).—The results of determinations of the amino-acid content of human blood, both normal and pathological (including diseases of the liver), give no support to the view that the liver plays an important part in intermediary protein metabolism. Determinations of the amino nitrogen content of the blood following ingestion of amino-acids are of no value as tests of liver function. E. S.

Possible Significance of Hexosephosphoric Esters in Ossification. IV. Phosphoric Esters of the Blood. H. W. GOODWIN and R. ROBISON (*Biochem. J.*, 1924, **18**, 1161—1162).—Two phosphoric esters were isolated from the blood. One of these reduces Fehling's solution and is lævorotatory. It is hydrolysed by the bone enzyme. The other does not reduce Fehling's solution and is not acted on by the enzyme. S. S. Z.

Rate of Elimination of Inorganic Salts from the Blood Stream. O. BARKUS (*Amer. J. Physiol.*, 1924, **69**, 35—40).—After intravenous injection, chlorides disappeared from sheep's blood almost immediately, phosphates first rapidly and then slowly; results with sulphates were untrustworthy.

CHEMICAL ABSTRACTS.

Carbohydrate Metabolism. I. Variations in the Nature of the Blood-sugar. L. B. WINTER and W. SMITH (*Proc. Roy. Soc.*, 1924, **B**, **97**, 20—40).—Normal blood filtrates have a lower rotation than would be expected from their copper-reducing power on the assumption that the reducing substance present consists solely of an equilibrium mixture of α- and β-glucose; the rotation, however, slowly increases and in 3 to 4 days corresponds with the reducing power. Filtrates from the blood of diabetics, on the other hand, have a high rotation which remains constant or diminishes only slightly. After mild hydrolysis (dilute hydrochloric acid), the rotation and reducing power of the normal filtrates correspond, whilst this treatment increases the rotation without affecting the reducing power of diabetic filtrates.

After injection of either thyroid extract or adrenaline, the blood of rabbits resembles diabetic blood in the above respect, but behaves normally when these substances are injected successively, although there is an increase in total blood-sugar. The blood of rabbits in convulsions due to insulin has a low rotation and no reducing power; the convulsions are relieved by adrenaline alone or by a mixture of thyroid and adrenaline. The mechanism of the action of insulin is discussed. E. S.

Hyperglycæmia after Parenteral Administration of Protein. W. LAUFBERGER (*Z. ges. exp. Med.*, 1924, **39**, 487—494; from *Chem. Zentr.*, 1924, i, 2794).—Intravenous injection of minimal amounts of protein causes hyperglycæmia in rabbits. The course of the hyperglycæmia varies with the protein used. Caffeine does not cause an appreciable hyperglycæmia in spayed females. G. W. R.

Effect of Ultra-violet Light on the Content of Fat and Sugar in the Blood of Animals deprived of Vitamins. D. ALPERN (*Strahlentherapie*, 1923, **15**, 661—666; from *Chem. Zentr.*, 1924, i, 2887).—The water and sugar in the blood of normal animals increase as the result of ultra-violet radiation. Less marked results are obtained in the case of the fat content. There is generally an increase in the light petroleum and ethyl alcohol fractions without corresponding increase in the cholesterol content. The blood of animals deprived of vitamins exhibits the same changes. G. W. R.

Alcohol. I. Determination of Ethyl Alcohol in Blood. H. KIONKA and P. HIRSCH (*Arch. exp. Path. Pharm.*, 1924, **103**, 282—294).—The alcohol is removed from the blood by distillation at 40° under diminished pressure, using an efficient condensing arrangement, and its content in the distillate determined by means of an interferometer. E. S.

Alcohol. II. Alcohol Content of Human Blood in the Fasting Condition, and after Ingestion of Carbohydrates or of Small Amounts of Alcohol. G. KÜHN (*Arch. exp. Path. Pharm.*, 1924, **103**, 295—312).—Values varying between 0·0006 and 0·0051% were found for the alcohol content of the blood of fasting individuals. No regular variations in these values were observed following a carbohydrate meal. Ingestion of small amounts of alcohol (two glasses of beer) together with a meal poor in carbohydrates, however, produced uniform increases which reached a maximum in about an hour. E. S.

Effect of Cations on Red Blood-corpuscles. W. ASHBY (*Amer. J. Physiol.*, 1924, **68**, 250—261, 585—610, 611—621).—Chlorides of sodium, magnesium, calcium, strontium, and barium increase, and of potassium and lithium decrease the resistance of human red blood-corpuscles to hypotonic sodium chloride solution. It is suggested that potassium can combine with the substance of the corpuscle in a manner different from that of

sodium. Changes produced by calcium and magnesium are not accounted for by loss of potassium. The red corpuscles of rabbit's, horse's, and pig's blood, having a high potassium content, behave similarly; those of cat's, dog's, and steer's blood, in which sodium predominates, are affected by univalent cations in the reverse manner, but as before with magnesium and calcium. It is argued that the distribution of sodium and potassium between cells and serum must be due to specific mutual relationships between the ion and cell-substance. CHEMICAL ABSTRACTS.

Changes in p_H of Blood with Coagulation. E. F. HIRSCH (*J. Biol. Chem.*, 1924, **61**, 795—805).—In the process of clotting blood becomes more acid, the average decrease in p_H observed being 0·09. It is suggested that the normal process of clotting may be brought about by changes in reaction following changes in the tension of carbon dioxide. C. R. H.

Blood Coagulation, Anti-coagulants, and Hæmolysis. J. W. PICKERING and F. E. TAYLOR (*Proc. Roy. Soc.*, 1924, **B**, **97**, 1—19).—A parallelism exists between hæmolysis and the inception (*i.e.*, the pre-clot phase) of the clotting of blood. Thus, potassium oxalate and sodium citrate inhibit the hæmolytic actions of heterologous sera, a specific hæmolysin, and cobra venom; this inhibition is removed by calcium chloride, which also restores coagulability. Too large a concentration of calcium chloride, however, inhibits hæmolysis, but it is also known to prevent coagulation. Other anti-coagulants (Witte's peptone, leech extract, neutralised thymus- and yeast-nucleic acids, novarsenol) which inhibit the pre-clot phase also restrain the hæmolytic actions of the above substances. Further examples are discussed in the original. These results are interpreted in favour of the theory of the coagulation of blood advanced by Pickering and de Souza (*Biochem. J.*, 1923, **17**, 747). E. S.

Hæmolytic Action of the Soaps. E. PONDER (*Biochem. J.*, 1924, **18**, 845—851).—The stearates, palmitates, and oleates are hæmolytic. The stearates are the least and the oleates the most active in this respect. The changes of shape of the erythrocytes are very similar to those produced by saponin and by bile salts. This lytic action of soaps is inhibited by the presence of serum, plasma, and a solution of hæmoglobin, especially in the case of oleates. If, however, these substances are added to the soap after this has been allowed to act on the cells a slight acceleration in the lytic action may be effected. Sodium and potassium soaps behave similarly. The time–dilution curves are logarithmic, whilst the time–temperature curves are hyperbolic. The percentage hæmolysis curve of sodium oleate (the only soap with which these observations can be made) is of the sigmoid type and shows, when suitable concentrations are used, a slight positive skewness. Solutions of the soaps tend to lose their hæmolytic power on keeping. S. S. Z.

Colorimetric Determination of Blood p_H at Body Temperature. A. B. HASTINGS and J. SENDROY, jun.—(See ii, 869.)

Determination of Gases in Blood and other Solutions by Vacuum Extraction and Manometric Measurement. I. D. D. VAN SLYKE and J. M. NEILL. **II.** C. R. HARINGTON and D. D. VAN SLYKE.—(See ii, 872.)

Determination of Carbon Dioxide in Serum in presence of Ether. J. H. AUSTIN.—(See ii, 873.)

Micro-determination of Proteins in Blood-serum. W. BERGER and L. PETSCHOCHER.—(See ii, 636.)

Determination of the Protein Fractions in Serum and Plasma. H. W. KNIPPING and H. L. KOWITZ.—(See ii, 636.)

Rôle of Phosphates in Carbohydrate Metabolism. I. Action of the Muscle Enzyme on the Organic Phosphorus Compounds of Blood. II. Effect of Insulin Administration on the Distribution of Phosphorus Compounds in Blood and Muscle. H. D. KAY and R. ROBISON (*Biochem. J.*, 1924, **18**, 1139—1151).—From experiments with muscle enzyme, which hydrolyses hexosediphosphoric but not hexosemonophosphoric ester, on the phosphoric esters of blood it is concluded that a hexosediphosphoric ester may be present in the blood; the evidence, however, is not entirely conclusive. The greater part of the organic phosphate of the blood, which is hydrolysable by the bone enzyme, is not hydrolysed by muscle (this vol., i, 904). Evidence is produced that after the administration of insulin organic phosphoric esters are synthesised in the corpuscles at the expense of the inorganic phosphate originally present in the blood plus additional phosphate drawn from other tissues. These esters are chiefly of the type not hydrolysed by the bone enzyme, but it is probable that sugar or a sugar derivative enters into their molecule, and on the basis of 1 mol. of dextrose per atom of phosphorus, the phosphoric acid thus esterified would account for nearly 40% of the sugar simultaneously disappearing from the blood. No changes are found in the amount of inorganic phosphate or total acid-soluble phosphorus in muscle, following insulin administration, but there is a marked increase (50%) in the amount of phosphoric esters ("lactacidogen-P") hydrolysed during 3 hours' autolysis of the macerated muscle at 38°. The phosphate for this increased "lactacidogen" is apparently drawn from the muscle. There is no evidence as to the origin of the carbohydrate portion of the molecule, but it accounts for more than seven times the amount of dextrose which disappears from the blood. S. S. Z.

Relationship of Phosphates to Carbohydrate Metabolism. I. Time Relationship of the Changes in Phosphate Excretion caused by Insulin and Sugar. S. S. SOKHEY and F. N. ALLAN (*Biochem. J.*, 1924, **18**, 1170—1184).—The administration of insulin to normal animals results in an immediate reduction in the excretion of inorganic phosphate and ammonia and in the titratable acidity of the urine. The nitrogen excretion in these circumstances increases in the first 6 hours after the administration of the insulin,

whilst the excretion of creatinine is unaffected. The volume of the urine is usually diminished in the first 3- or 6-hour periods after insulin and is followed by a compensatory increase usually appearing in the post-hypoglycæmic period. The administration of sugar induced an increased excretion of phosphate, but a decrease in the excretion of nitrogen. The joint effect of insulin and sugar brings about a decrease in the phosphate and nitrogen excretion. The administration of acid does not alter the excretion of phosphate. The phosphorus excretion of diabetic dogs without insulin is very high. Administration of insulin causes a decrease in the excretion, then an increase, with return to the level for a normal dog. These changes are discussed and their significance is suggested.

S. S. Z.

Acid–Base Exchanges in Mammalian Voluntary Muscle. S. Andrews, F. Beattie, and T. H. Milroy (*Biochem. J.*, 1924, **18**, 994—1008).—In the expressed juice from frozen muscle there are present at least three systems which carry base in a readily disposable form, namely, the inorganic phosphates, the organic phosphate precursors, and the colloidal or protein salts. When lactic acid is produced as a result of heating the juice, the acid secures its base from all these systems, the buffering capacity depending especially on the base derivable from the hydrolysed organic phosphate precursor, and also from the constituents of the juice which do not pass into the ultrafiltrate. If there is no inorganic phosphate increment accompanying the acid production, the buffering capacity is diminished, as the sole base-carrying systems which are then in evidence are the pre-formed inorganic phosphates and the proteins. S. S. Z.

Antiketogenesis. V. Ketolytic Reaction. Action of Glycollaldehyde and of Glyoxal. P. A. Shaffer and T. E. Friedemann (*J. Biol. Chem.*, 1924, **61**, 585—623; cf. A., 1921, i, 754; 1923, i, 166).—Glycollaldehyde, like dextrose, has the power of accelerating the oxidation of acetoacetic acid by hydrogen peroxide in alkaline solution. The previous view that the ketolytic reaction consisted in the condensation of an intermediate oxidation product of dextrose with acetoacetic acid with the formation of a readily oxidisable product, led to similar experiments with glyoxal, which is known to be an intermediate product in the course of the oxidation of glycollaldehyde to formic acid. Owing, however, to the extreme rapidity with which glyoxal is oxidised in alkaline solution, it does not, under these conditions, condense with acetoacetic acid, and therefore cannot act ketolytically. It is therefore necessary to assume that the ketolytic power of glycollaldehyde is due to the condensation of the aldehyde itself with acetoacetic acid, probably by Knoevenagel's reaction (A., 1898, i, 446), the condensation being accelerated by the rapid oxidative removal of the product. The hypothesis is supported by a quantitative analysis of the products of the ketolytic reaction; this analysis further indicates that 2 mols. of acetoacetic acid condense with 1 mol. of glycollaldehyde. It is suggested that the ketolytic action

of dextrose may similarly be due to the direct condensation of the hexose itself, by virtue of its aldehydic properties, with 2 mols. of acetoacetic acid. C. R. H.

Synthesis of Menthol-glycuronic Acid in the Rabbit. A. J. QUICK (*J. Biol. Chem.*, 1924, **61**, 679—683).—After administration of small doses of menthol to rabbits almost 50% is excreted in the form of menthol-glycuronic acid; the amount conjugated decreases as the dose approaches the lethal amount. During prolonged administration of sub-lethal doses, the daily excretion of menthol-glycuronic acid remains practically constant. C. R. H.

Decomposition of Sugar in the Lungs. E. SLUITER (*Arch. Néerland. Physiol.*, 1924, **9**, 461—479).—Perfusion experiments with blood containing added dextrose show that the sugar content of the blood falls for a time and then remains nearly constant; the failure to fall to a lower level may be due to the change of p_H of the blood caused by the production of lactic acid, inhibiting further glycolysis. The amount of sugar disappearing is not proportional to its concentration in the blood, nor does it give rise to the theoretical quantity of lactic acid. H. J. C.

Influence of "Collargol Blockade" of the Liver on Intermediary Metabolism. SUGANUMA (*Biochem. Z.*, 1924, **144**, 141—146).—Observations have been made of the effect of intravenous injections of collargol on the hepatic functions of starving dogs. The secretion of bile is diminished but later returns to supra-normal levels. The sugar and amino-acid content of the blood are increased; the former, however, becomes sub-normal before returning to normal values. Collargol injection lowers the urea content of the blood. The rise in blood-sugar is ascribed to stimulation of the liver cells, whilst the decreased blood-urea follows on the inhibition of the "star" cells of Kupfer. J. P.

Relation of Arginine and Histidine to Growth. W. C. ROSE and G. J. COX (*J. Biol. Chem.*, 1924, **61**, 747—773).—Rats fed on a diet of which the sole source of nitrogen is completely hydrolysed casein grow at a slower rate than those fed on the unhydrolysed protein; if the hydrolysis products are treated with silver sulphate and barium hydroxide to remove arginine and histidine, the residual mixture of amino-acids does not suffice for growth or maintenance of weight. The addition of 0·1 g. of histidine monohydrochloride per 100 g. of food to the diet, which had been made deficient by the above treatment, restores its growth-promoting properties, whereas the addition of even large amounts of arginine does not do so. The latter observation is in contradiction to the conclusions of Ackroyd and Hopkins (A., 1917, i, 237) regarding the interchangeability of arginine and histidine in metabolism. C. R. H.

Comparative Ability of Deficient Proteins and Ammoniacal Organic Salts partially to Satisfy the Minimum Nitrogen Requirements. E. F. TERROINE, P. FLEURET, and T. STRICKER (*Arch. Intern. Physiol.*, 1923, **22**, 43—86).—During the adminis-

tration of a nitrogen-free diet, preceded by injection of ammonium salts, the nitrogen excreted was of the same order as that obtained when gelatin had been given. The economy value resultant from ammonium salts when the minimum nitrogen reserve is used up is smaller than that from gelatin, probably on account of the presence of some amino-acids. The amount of nitrogen necessary for endogenous metabolism can be regarded as the sum of (*a*) the amount of "differentiated" nitrogen in the form of amino-acids, and (*b*) that of "undifferentiated" nitrogen (of ammonia), often masked by nitrogen of amino-acids or ammonium salts.

CHEMICAL ABSTRACTS.

Changes in the Lime Content of the Hen's Egg during Development. R. H. A. PLIMMER and J. LOWNDES (*Biochem. J.*, 1924, **18**, 1163—1169).—Shell-less eggs contain more than sufficient lime for the needs of the developing chick. The lime content of eggs increases during the development of the chick; it enters the egg from the shell. A similar increase occurs in pigeons' eggs during development. S. S. Z.

"Lecitiburin," a Lecithin from the Eggs of the Shark. H. P. PONCE (*Anál. Asoc. Quím. Argentina*, 1924, **12**, 5—12).—A note describing the preparation from the eggs of the shark of a lecithin, m. p. 70°, to which the name "lecitiburin" is given.

G. W. R.

Chemical Composition of Edible Viscera from Meat-producing Animals. W. C. POWICK and R. HOAGLAND (*J. Agric. Res.*, 1924, **28**, 339—346).—Analyses are recorded of edible viscera of steers, pigs, calves, and lambs. In general, the food values depend mainly on the protein content. Livers corresponded closely with lean beef in nitrogen content, but other organs were inferior in this respect. With the exception of hearts, tongues, lungs, and stomachs, the organs examined usually contained more phosphorus than lean beef. [Cf. *B.*, 1924, 961.] A. G. P.

Determination of Glycogen in the Placenta. R. CLOGNE, (MLLE.) WELTI, and M. PICHON (*Bull. Soc. Chim. biol.*, 1924, **6**, 788—790).—Determinations of placental glycogen by the method of Bierry and Gruziewska, and by an improved modification of this method, give values varying between 0·60 and 1·66%. J. P.

Cholesterol Content of the Bile, Blood, and Flesh of the Hippopotamus. J. A. GARDNER (*Biochem. J.*, 1924, **18**, 777—784).—The bile of the hippopotamus contains both free and ester cholesterol to the extent of 0·47% of the solid matter. Small quantities of free and ester cholesterol were also found in the blood and in the flesh of this animal. S. S. Z.

Inositol. II. Synthesis of Inositol in the Animal Body. J. NEEDHAM (*Biochem. J.*, 1924, **18**, 891—904).—The animal body seems to possess the power of synthesising inositol. Rats fed on an inositol-free diet for 8 months contained the normal amount of

free inositol. No diminution in the body-content of inositol was observed when a lasting and vigorous excretion of the compound was induced in rats subsisting on an inositol-free diet. S. S. Z.

Uric Acid in the *Pieridæ*: Quantitative Study. V. B. Wigglesworth (*Proc. Roy. Soc.*, 1924, **B**, **97**, 149—155).—In *Pieris brassicæ*, the wings of the male contain more uric acid than do those of the female. This difference is attributed to the greater size of the wing scales which cover the androconia of the male. The total amount of uric acid is unchanged during pupal life. The *Pieridæ* appear to differ from other families in the use to which uric acid is put rather than in the amount produced. O. O.

Bioluminescence. V. Luciferin of *Cypridina Hilgendorfii*. S. Kanda (*Amer. J. Physiol.*, 1924, **68**, 435—443).—The methyl-alcoholic extract of *Cypridina* is evaporated to a small volume, ethyl alcohol is added, the liquid filtered, and the filtrate evaporated to dryness. The residue is dissolved in distilled water saturated with hydrogen, and the luciferin is completely precipitated on saturation with ammonium sulphate. The precipitate after rapid drying is again extracted with water saturated with hydrogen, or with absolute methyl or ethyl alcohol. The luciferin, the presence of which is indicated by the production of light with *Cypridina* luciferase, gives Molisch's reaction, but neither Millon's nor the ninhydrin reaction. It is not precipitated by acids, alkalis, or salts other than ammonium sulphate; results obtained with alkaloidal reagents were not conclusive. A. A. E.

Circulation of Lead in the Organism Investigated by a Radio-chemical Method. I. A. Christiansen, G. Hevesy, and S. Lomholt (*Compt. rend.*, 1924, **179**, 291—293).—Lead hydroxide mixed with olive oil containing a little lamp-black and some radium-*D* was injected into rabbits and guinea-pigs. A diagram is given showing lead distribution in fæces, urine, and viscera together with that found at the point of injection. The proportion of lead found in the liver and fæces is greater whilst that in the kidneys and urine is less than in the case of bismuth. H. J. E.

Micro-determination of Silicon and its Concentration in certain Organs. G. Bertrand.—(See ii, 872.)

Determination of Cystein. Y. Okuda.—(See ii, 792.)

Determination of Cystine. Y. Okuda.—(See ii, 793.)

Mammary Secretion. V. I. Further Research on the Threshold and Effects of Protein "Excess." II. Quantitative Relation of Vitamin-*B* to Protein. G. A. Hartwell (*Biochem. J.*, 1924, **18**, 785—794).—A high proportion of protein in the diet of the lactating rat produces an abnormal condition in the young. There is, however, a quantitative relationship between protein and vitamin-*B* in the diet; if the latter is increased when the protein is increased no evil results ensue, but the rate of growth of the suckling is impaired. The function of vitamin-*B* is primarily

concerned with the metabolism of protein or with the nitrogen part of the protein molecule. S. S. Z.

Mineral Content of Human Milk in Normal and Rachitic Families. S. V. TELFER (*Biochem. J.*, 1924, **18**, 809—813).—No appreciable differences were found in the composition of the milks of women whether the infants developed rickets or not. S. S. Z.

Organic Constituents of Saliva. H. UPDEGRAFF and H. B. LEWIS (*J. Biol. Chem.*, 1924, **61**, 633—648).—A modification of the technique of Folin and Wu (A., 1919, ii, 308) is described, which is suitable for the removal of proteins from saliva, and the average concentrations of the non-protein nitrogenous constituents of normal saliva have been determined and compared with corresponding figures for blood. The total non-protein nitrogen of saliva is 37% of that of blood, but the relationship between the individual constituents is different in the two fluids, *e.g.*, in saliva there is relatively much ammonia and urea and practically no amino-acid nitrogen. C. R. H.

Analysis of Urine. MAX WEINTRAUT (*Arch. Pharm.*, 1924, **262**, 360—368).—A discussion of the determinations necessary for diagnostic purposes, and of the results produced by various pathological conditions. B. F.

Exchanges of the Blood and the Excretion of Urobilin. G. KÜHL (*Arch. exp. Path. Pharm.*, 1924, **103**, 247—259).—Contrary to Whipple's view (*Arch. intern. Med.*, 1922, **29**, No. 6), the urobilin excreted in the urine and fæces is derived solely from the destruction of hæmoglobin. When injected into normal dogs, hæmoglobin is converted quantitatively into urobilin and excreted as such; in anæmic animals, however, part of the hæmoglobin is retained. Following loss of hæmoglobin (withdrawal of blood), the excretion of urobilin falls below the normal. E. S.

Photochemical Reaction of Urine. A. VON SOÓS (*Z. klin. Med.*, 1924, **98**, 347—352; from *Chem Zentr.*, 1924, **i**, 2789).—In dark urines, substances are found which inhibit the action of photographic developers on silver chloride which has been exposed to light. This effect is attributed to protective colloids. G. W. R.

Effect of Alcoholic Extract of Commercial Dextrose on Urinary Reducing Substance. C. C. WANG and A. R. FELSHER (*J. Biol. Chem.*, 1924, **61**, 659—665).—Ingestion of commercial dextrose causes a greater excretion of reducing substances than does the same weight of pure dextrose; the effect is due to an unidentified constituent of the commercial preparation which can be extracted therefrom with alcohol. The extract alone produces no excretion of reducing substance. C. R. H.

Rapid Determination of Lead in Urine. L. J. FAIRHALL.—(See ii, 873.)

Determination of Mentholglycuronic Acid in Urine. A. J. QUICK.—(See ii, 876.)

Direct Nesslerisation Micro-Kjeldahl Method and a Modification of the Nessler-Folin Reagent for Ammonia. F. C. Koch and T. L. McMeekin.—(See ii, 871.)

Glycolytic Properties of the Cancer Cell. N. Waterman (*Arch. Néerland. Physiol.*, 1924, **9**, 573—587).—Warburg's observation that the glycolytic power of carcinoma tissue from a rat was abnormally high has been confirmed for several types of tumour (man and rats) by measuring the carbon dioxide displaced from a Ringer solution containing added dextrose and excess of sodium hydrogen carbonate. The effect of calcium salts on this glycolysis has been studied and the lactic acid produced has been determined. It is found that normal pancreatic tissue from several types of animal possesses a definite though much smaller power to convert sugar into lactic acid. Attempts to raise the glycolytic power of normal tissue to the high level of that of tumour tissue (kidney tissue with its very low glycolytic power was used) were made; addition of phosphates to the Ringer solution was without effect: hexosephosphate gave inconclusive results; extraction of triturated carcinoma tissue with physiological saline and addition of the extract to the medium caused a rise in glycolytic action in some cases. H. J. C.

Calcium Content of the Blood-serum in Cases of Gout. V. Coates and P. C. Raiment (*Biochem. J.*, 1924, **18**, 921—924).—There is a considerable rise in the calcium of the blood-serum in cases of gout. S. S. Z.

Chemical and Physico-chemical Changes in Blood in Experimental Nephritis. J. Mosonyi (*Z. klin. Med.*, 1924, **99**, 500—505; from *Chem. Zentr.*, 1924, i, 2788).—After poisoning with cantharidin, the elimination of nitrogen in dogs remains normal. The freezing point of the blood rises to −0·512° and then sinks gradually to normal. After uranium poisoning, marked nitrogen retention occurs and the freezing-point of the blood rises to −0·53°, then falls to −0·638°, and subsequently becomes normal after repeated small rises. Mercuric chloride poisoning causes at first an increase in the nitrogen content of the blood. After 7 days, the residual nitrogen falls considerably below normal, and remains at this level until the end of the illness. G. W. R.

Nephropathic Action of the Dicarboxylic Acids and their Derivatives. I. Tartaric, Malic, and Succinic Acids. II. Glutaric and Malonic Acids. W. C. Rose (*J. Pharm. Exp. Ther.*, 1924, **24**, 123—146, 147—158).—The acids were administered subcutaneously to rabbits and their effect on renal activity determined by analyses of the blood constituents and by the phenolsulphonephthalein test; in a few cases, histological examinations of the kidneys were made. Tartaric and glutaric acids exerted a pronounced, and *dl*-malic acid a slight nephropathic action, while *l*-malic, succinic, and malonic acids were inactive. The renal-toxic action of certain acids appears to be associated with their slow oxidation in the organism. From the fact that calcium

glutarate has a greater solubility than calcium succinate it is concluded that the toxicity of the glutarates is not due to the deposition of the insoluble calcium salt in the kidney. E. S.

Relation of the Fat-soluble Factor to Rickets and Growth in Pigs. III. S. S. ZILVA, J. GOLDING, J. C. DRUMMOND, and V. KORENCHEVSKY (*Biochem. J.*, 1924, **18**, 872—880).—Rickets characterised by the presence of significant amounts of osteoid tissue can be induced in pigs on a diet in which dried separated milk is the main source of the fat-soluble vitamins. S. S. Z.

Chemical Basis for the Treatment of Tuberculosis. Action of Steapsin and Insulin on Tubercle Bacilli. L. G. ROBINOVITCH and G. W. STILES (*Amer. Rev. of Tuberculosis*, 1924, **9**, 587—612).—Lipase in alkaline solution to which is added a "cohydrolyser" of bees-wax (chloroform), acts as a decorticator of tubercle bacilli, presumably by hydrolysing the lipoid outer membrane. Insulin produces the same effect as lipase. J. P.

Action of Alkaloids on the Field-locust (*Acrididæ*). R. BECKER (*Arch. exp. Path. Pharm.*, 1924, **100**, 335—348).—The pharmacological actions of alcohol, ethereal oils, chloroform, xylene, benzene, acids, alkalis, and salts on the female of the field-locust are briefly recorded. At greater length are described investigations on the action of alkaloids, including physostigmine, veratrine, cocaine hydrochloride, nicotine, caffeine–sodium salicylate, morphine hydrochloride, arecoline hydrobromide, pilocarpine hydrochloride, and also of mixtures of these alkaloids. Similar effects to those obtained by the alkaloids, *i.e.*, paralysis, vibration of the jumping legs, etc., are obtained by the application of heat.
W. O. K.

Action of Chemical Irritants on the Vitality of Protozoa, as Measured by the Rate of Division. H. HANDOVSKY, E. DU BOIS-REYMOND, and C. M. VON STRANTZ (*Arch. exp. Path. Pharm.*, 1924, **100**, 273—287).—Cantharidin, undecylenylvanillylamide, amyl nitrite, and arsenious oxide usually inhibit the rate of division of *Balantiophorus minutus*. Histamine hydrochloride inhibits it at first and then later accelerates it. Cantharidin and arsenious oxide appear occasionally to have a stimulating action on some of the cells of a culture. W. O. K.

Action of Some Compounds on the Excitability of the Nervus Ischiadicus of the Frog. H. HANDOVSKY and R. ZACHARIAS (*Arch. exp. Path. Pharm.*, 1924, **100**, 288—293).—Morphine hydrochloride, chloral hydrate, alcohol, urethane, camphor, cocaine hydrochloride, veratrine, strychnine nitrate, and hydrogen peroxide increase in low concentration and decrease in high concentration the excitability of the nervus ischiadicus of the frog. Phenol, antipyrine, and novocaine were depressants, and caffeine an excitant, at all concentrations tested. Arsenious oxide was without effect. The inorganic ions present also influence the excitability, the potassium ion tending to increase it. W. O. K.

Leucocytogenic Properties of Copper Potassium Cyanide. E. TROCELLO (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 148—167; from *Chem. Zentr.*, 1924, i, 70).—Intravenous injection of a 0·2% aqueous solution of "cuprocyan" results in an increase in the number of leucocytes in the blood of rabbits. The effect is partly shown by the lymphocytes. G. W. R.

Pharmacological Investigations on Iron: Colloidal Ferrous Sulphide prepared in Presence of Gelatin. II. Experiments on Rabbits by Intravenous Injections. L. SABBATANI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 473—479).—The effects on rabbits of intravenous injections of the colloidal ferrous sulphide prepared by the method previously elaborated (this vol., ii, 116) are described. Whether *in vitro* or *in vivo* or in tissues isolated from the dead body, the sulphide passes into hydrated ferric hydroxide, which remains tenaciously held at the point where the sulphide was first fixed and is difficult to observe, as its colour is easily confused with that of the tissues themselves. T. H. P.

Pharmacological Investigations on Iron. V. Colloidal Ferrous Sulphide prepared in Presence of Gelatin. L. SABBATANI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 8—13; cf. this vol., ii, 116, and preceding abstract).—Details are given of the effects produced in dogs by intravenous injection of colloidal ferrous sulphide prepared in presence of gelatin. T. H. P.

Induced Oxidation and the Explanation of the Internal Use of Iron Salts and of Fever. N. R. DHAR (*J. Physical Chem.*, 1924, **28**, 943—947).—The induced oxidation of fats, proteins, sugars, etc. by air at the ordinary temperature in the presence of sodium sulphite or of freshly-precipitated ferrous hydroxide (T., 1917, **111**, 690; A., 1921, ii, 36, 37, 391; 1922, i, 1210) is regarded as a close analogue of the processes which occur in the body. Fever is described as an auto-catalytic reaction accelerated by foreign substances, *e.g.*, bacterial secretions. S. S.

"Nitritoid Crisis" Produced by Arsenobenzene Derivatives. VI. Experiments on Isolated Organs with Plain Muscle. A. BUSACCA (*Arch. Farm. sperim. Sci. aff.*, 1924, **23**, 58—71).—Neosalvarsan in 0·01% solution is without effect on vascular musculature of isolated lung, which is without sympathetic innervation. In 0·01% solution, it produces enlargement of the pupil of the isolated eye of a frog, whilst at higher concentrations it acts as a local caustic and produces constriction. In 0·02% solution neosalvarsan and oxidised neosalvarsan stimulate motility in the plain muscle of certain human organs. With higher doses this effect is maintained in the case of neosalvarsan, whilst in the case of oxidised neosalvarsan, a depressant effect is produced. Neosalvarsan in therapeutic doses stimulates the terminal fibres of the sympathetic system, and it is suggested that this system is involved in the "nitritoid crisis." G. W. R.

Toxicity of Chaulmoogra Oil. B. E. Read (*J. Pharm. Exp. Ther.*, 1924, **24**, 221—258).—Ethyl hydnocarpate causes the same disturbances as the oil and hydnocarpic acid as the ethyl or glyceryl ester, or salt, appears to be the most active constituent of preparations of the oil. Toxic doses of hydnocarpates cause hæmolysis, renal irritation, and fatty infiltration of the liver. Increased lymph flow follows intravenous injection of ethyl hydnocarpate. Administered in this way, it kills rabbits in a dose of 0·5 c.c. per kg. body-weight, causing hypersensivity with lowered blood calcium, inco-ordinated movements, and finally death from respiratory failure. H. J. C.

Theory of Narcosis. M. Cloetta and H. Thomann (*Arch. exp. Path. Pharm.*, 1924, **103**, 260—281).—During narcosis with ether, alcohol, or "somnifen," the calcium content of the plasma of dogs is depressed (8—15%), the depression running parallel with the narcosis; corresponding with this depression, the potassium content of the plasma is increased. On the other hand, excitation with *ac*-tetrahydro-β-naphthylamine produces a rise in the calcium content. In conformity with these results, injection of substances which precipitate calcium (oxalates, phosphates) decreases the action of the above narcotics, the phosphates being the more effective in this respect. Administration of calcium increases the narcotic action in the case of frogs, but this effect has not been observed with dogs. No significant changes occur in the density, viscosity, or protein content of the plasma during narcosis, nor is the stability of the plasma colloids towards increases in temperature or changes in the concentration of ions altered; the surface tension, however, usually decreases slightly, but it is doubtful if this is of significance for narcosis. These results suggest that narcotics produce a disturbance in the ionic equilibrium in the brain and perhaps in other organs. E. S.

Narcotic Leucocytosis. Experimental Researches on Guinea-pigs. R. Seyderhelm and E. Homann (*Arch. exp. Path. Pharm.*, 1924, **100**, 322—334).—Ether, chloroform, ethyl chloride, ethyl bromide, chloral hydrate, urethane, alcohol, sulphonal, and morphine, which induce narcosis when administered to a guinea-pig, also cause a marked leucocytosis in that animal, whilst scopolamine, which does not cause narcosis in the guinea-pig, does not give rise to a leucocytosis. There would therefore appear to be a definite leucocytosis, associated with the effect of drugs causing narcosis. W. O. K.

Comparative Toxicity of Novocaine, Neocaine, Procaine, and Apothesine. Effect of Intravascular Injections. W. R. Meeker and E. B. Frazer (*J. Pharm. Exp. Ther.*, 1924, **22**, 375—392).—Novocaine (German), and the corresponding products, neocaine (French) and procaine (American), have equal toxicity as determined by the minimum lethal dose on intravenous injection into rabbits under uniform conditions, and are equally effective as local or regional anæsthetics. The American product "apothesine" is more toxic. W. O. K.

Study of Two Series of Procaine Derivatives with Reference to the Relationship between their Pharmacological Action and Chemical Constitution. H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 159—166).—Determinations have been made of the relative anæsthetic activities and toxicities of various substituted aminoethanol and aminopropanol esters of *p*-aminobenzoic acid, using the rabbit's cornea for the former measurements, and mice for the latter. In both series, the anæsthetic activity increased with increase in the size of the substituent alkyl groups, the *iso*propyl compounds being more active than the *n*-propyl compounds. The toxicity, however, also increased. In the aminoethanol series this increase was proportional to the increase in anæsthetic activity, whilst in the case of the aminopropanol series it was greater than the anæsthetic activity. Hence, although the members of the latter series have greater anæsthetic activities than those of the former, their therapeutic indices are smaller.

E. S.

Local Anæsthetic Properties of *p*-Aminobenzoyldi*iso*propylaminoethanol Hydrochloride ("Isocaine"), Cocaine, Procaine, and Butyn. H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 167—177).—"Isocaine" has approximately the same efficiency as cocaine in anæsthetising the cornea and only three-tenths of its toxicity. It is twice as toxic as procaine, and hence is less suitable for paralysis of sensory nerve trunks, although it has about the same efficiency as the latter substance for this purpose. Butyn has ten times the toxicity of procaine; it is more efficient (but more toxic) than cocaine in anæsthetising the cornea, and only half as efficient as procaine for paralysis of sensory nerves. The minimum lethal doses of the drugs differ with different species.

E. S.

Colloid Chemistry of Protoplasm. III. Viscosity of Protoplasm at Various Temperatures. IV. Heat of Coagulation of Protoplasm. L. V. HEILBRUNN (*Amer. J. Physiol.*, 1924, **68**, 645—648; **69**, 190—199).—III. Maximal viscosities were observed in the protoplasm of the egg of the clam *Cumingia* at 2°, 15°, and 30°.

IV. The temperature of coagulation of the protoplasm of sea urchin and *Cumingia* eggs is below that of proteins, but the coefficient is similar. The coagulation of protoplasm is probably associated with a change in the physical state of the emulsified fats.

CHEMICAL ABSTRACTS.

Biochemistry of Skin and the Chemical Basis of Skin Swelling. M. KAYE and D. J. LLOYD (*Biochem. J.*, 1924, **18**, 1043—1057).—There is an absolute identity of the conditions producing hardness in the interfibrillary fluid in which the fibrils and fibres of skin are embedded with those causing irreversible coagulation of proteins, and it is concluded that the cementing of the fibrils in some dried skins must be due to coagulation. Substances which disperse or destroy denatured albumin were also

found to remove the coagulated interfibrillary matter. The colloidal swelling of skins is due to the network of skin fibres which consist of collagen, and the swelling in acid and in alkaline solution is brought about by the formation of ionisable salts of collagen. The removal of free amino groups in the skin reduces the amount of acid absorbed and combined. The swelling in acid solution is due to the presence of free amino groups. S. S. Z.

Nature of Fœtal Re-adsorption. N. H. Long and A. S. Parkes (*Biochem. J.*, 1924, **18**, 800—805).—Intra-uterine absorption of the fœtus is due to autolysis of the latter and not to the action of uterine enzymes. S. S. Z.

Autolysis. XII. Experimental Atrophy of Muscle Tissue. K. K. Chen, W. Meek, and H. C. Bradley (*J. Biol. Chem.*, 1924, **61**, 807—827).—During 9 weeks after section of the sciatic and femoral nerves in rabbits the muscles supplied by these nerves lost 50% in weight; they showed no increased water content. Such atrophic muscle contains the same amount of free amino-acids as healthy muscle and slightly more peptides; when subjected to sterile autolysis, it develops the same reaction as normal muscle but liberates more free amino-acids than the latter. It is suggested that this is due to a gradual alteration of the structural cell-proteins into a digestible form during the process of atrophy. C. R. H.

Effect of Heat on the Activity of the Peroxydase in Milk. G. Spitzer and M. C. Taylor (*J. Dairy Sci.*, 1924, **7**, 234—244).—By use of the Storch reaction in comparative experiments on various mixtures of sterilised with raw milk, it was shown that the greater part of the peroxydase is inactivated at 85°. The rate of inactivation is a function of the temperature and time of exposure and appears to follow a definite law. Chemical Abstracts.

Laws of the Action of Laccase: Influence of the Reaction of the Medium. P. Fleury (*Compt. rend.*, 1924, **179**, 709—711; cf. A., 1924, i, 594, 697, 921, 1144).—The optimum value of p_H for the action of laccase varies from 6·7 to 7·6 as the percentage of guaiacol initially present in the solution varies from 1 to 0·25. The action of the laccase is regarded as the resultant of two phenomena, one being the fixation of the guaiacol by the enzyme and the other its oxidation; the former of these becomes less, and the latter more intense as the value of p_H increases. T. H. P.

Oxydases. J. Clarens (*Bull. Soc. chim.*, 1924, [iv], **35**, 1198—1206).—Using the constant-volume ureometer previously described (Job and Clarens, A., 1909, ii, 826), the oxidation of quinol in alkaline solution has been studied by measuring the rate of absorption of oxygen. The oxidation is proportional to the alkalinity of the solution and, owing to the formation of acid oxidation products, the oxidation ceases when the acidity reaches a certain value. If the acidity is removed by the addition of calcium carbonate, the oxidation continues at a rate determined by the velocity of reaction of the calcium carbonate with the acid oxidation products. The velocity of oxidation is increased by the presence of manganous

salts. The acceleration is attributed to the power of manganese to form complexes with hydroxyl ions, thereby favouring the action of hydroxyl ions on the quinol in the presence of oxygen, a view supported by the fact that iron and copper salts similarly accelerate the oxidation. Oxidation in the presence of the oxydase of lucerne follows a different course. The oxidation products are not acid and the oxidation continues regularly; if the oxydase is destroyed by heat or by using very strongly alkaline solutions, the oxidation of the quinol continues until the alkalinity of the solution disappears owing to the formation of acid oxidation products, a certain number of hydroxyl ions being, however, immobilised in a complex with the the oxydase. This second mode of oxidation of quinol in presence of an oxydase is also catalysed by manganous salts. R. B.

Xanthine Oxydase. I. Preparation and Properties of the Active Material. M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 971—975).—Xanthine oxydase is associated with the caseinogen of milk, and a stable preparation can be obtained by treating the milk with an equal volume of saturated ammonium sulphate solution. The precipitated caseinogen and fat are then dried between filter-paper, thoroughly extracted with ether, and the residue is dried. The enzyme can be adsorbed from a neutral solution of this preparation almost completely by alumina and filter-paper. Charcoal adsorbs it only slightly. It is destroyed by alcohol and acetone and slowly by atmospheric oxygen. Ether, chloroform, toluene, and glycerol do not inactivate it. The presence of fat in a finely-divided state, as in milk, accelerates the action of the enzyme. Hypoxanthine and xanthine on keeping in neutral solution become incapable of oxidation by the enzyme. S. S. Z.

Xanthine Oxydase. II. Dynamics of the Oxydase System. M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 976—988).—The following results on the dynamics of xanthine oxydase have been obtained by employing the method of reducing methylene-blue to its leuco base in a vacuum. The reaction velocity is not affected by hydrogen-ion concentration between p_H 5·5 and 9. Above p_H 9 and below p_H 4, the enzyme is destroyed. Between p_H 4 and 5, the reaction velocity is very small, but no destruction occurs. The reaction velocity is directly proportional to the enzyme concentration, but is independent of methylene-blue concentration providing it is not very small. The reaction velocity is independent of purine-base concentrations up to a certain critical concentration, beyond which it decreases. This critical concentration becomes higher with increased enzyme concentration. Below the critical concentration of the substrate hypoxanthine reduces methylene-blue twice as fast as xanthine does, but as the inhibition begins the rates approach one another and become equal when inhibition is complete; the reaction velocity is then dependent on methylene-blue concentration. On addition of purines other than the substrate, the reaction velocity is also eventually decreased. The authors incline to the view that Schardinger enzyme and xanthine oxodase are identical. S. S. Z.

Xanthine Oxydase. III. Reduction of Nitrates. M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 989—992).—The "atite" of Haas and Hill (this vol., i, 349) is identical with the oxydase or oxydases of milk. Xanthine oxydase reduces nitrates to nitrites in the presence of hypoxanthine, xanthine, adenine, or aldehyde. The rate of reduction of nitrate is proportional to that of the reduction of methylene-blue under various conditions. The inhibitory effect of purines is also observed in this case (see preceding abstract). S. S. Z.

Phosphoric Esterase of Blood. M. MARTLAND, F. S. HANSMAN, and R. ROBISON (*Biochem. J.*, 1924, **18**, 1152—1160).—The inorganic phosphate in the laked whole blood and in laked corpuscles increases rapidly at first and then more slowly, until after 4 days it amounts to 93% of the organic acid-soluble phosphorus in both cases. The rate of hydrolysis is greater at a p_H slightly on the acid side of the normal blood reaction and close to the neutral point. The enzyme responsible for the hydrolysis is present in both plasma and corpuscles or is possibly adsorbed by the latter from the plasma. It resembles the muscle esterase in its ability to hydrolyse hexosediphosphoric esters and in its relative inactivity towards hexosemonophosphoric and glycerophosphoric esters. A portion of the esters hydrolysable by bone is also hydrolysed by the blood enzyme during the early stages of autolysis, but the remaining portion is very resistant. It is found that no significant change in the reducing power occurred during the early stages of the autolysis in laked blood or corpuscles, although 50% of the phosphoric esters might be hydrolysed. In the later stages of the hydrolysis, a rise of about 30% in the sugar value is usually observed. In unlaked whole blood at a p_H somewhat above normal, synthesis of phosphoric esters was observed; when the p_H rises above or falls below certain limits, the rate of hydrolysis of the phosphoric esters becomes greater than the rate of synthesis and the inorganic phosphate increases. At a p_H somewhat lower than 7·0, the rate of hydrolysis may approach that in laked blood. S. S. Z.

***A*. Use of Invertase. *B*. Repeated Use of the Same Preparation of Invertase.** E. K. O. SCHMIDT (*Z. Ver. deut. Zuckerind.*, 1924, **817**, 727—786).—*A*.—A solution of invertase prepared by the autolysis of yeast can be concentrated at 30°/30 mm. without much loss of activity. A study of the effect of invertase on solutions containing different concentrations of sucrose shows that the time required to reduce the rotatory power of the solution to zero increases with the concentration of sucrose, somewhat more slowly than the latter up to 20% sucrose, and more quickly between 20% and 50% sucrose. The optimum temperature for the action of yeast invertase is about 55°. The less pure the sugar, the less active is the invertase.

B.—At 55°, at which temperature zymase is destroyed, whole yeast can be used for the inversion of sucrose; it is possible, after inversion is complete, to remove the yeast by filtering the solution through a collodion filter and use it for the inversion of a second

lot of sucrose, or to make the process of inversion continuous by sucking the sucrose solution slowly through such a filter covered with a layer of yeast. Preparations obtained by the adsorption of invertase on charcoal are not suited for repeated use because the enzyme is readily dissolved out from the adsorbate, but the dried residue of a mixture of a solution of invertase with one of gelatin can be used for the inversion of at least eleven successive quantities of sucrose without loss of activity. C. R. H.

Mode of Action of Invertase. H. VON EULER and K. JOSEPHSON (*Arkiv Kemi, Min., Geol.*, 1924, **9**, No. 4, 1—6).—It is calculated that for invertase $k_a=10^{-7}$, $k_b=10^{-11}$, with the isoelectric point about $p_H=5$; viscosity measurements show a minimum at $p_H=4$—5. Reaction-producing molecules of catalyst+substrate are postulated, their formation and decomposition discussed, and their concentration is estimated at 10^{-8} for 0·1*N*-sucrose. The activity–p_H curve is said to be almost identical with that of raffinase on the alkaline side of the optimum. [Cf. *B.*, 1924, Dec. 26.] F. M. H.

Properties of a Highly Active Invertase Preparation. K. MYRBÄCK (*Arkiv Kemi, Min., Geol.*, 1924, **9**, No. 2, 1—6).—A highly purified stable invertase (*If*=240) was prepared (cf. *B.*, 1924, Dec. 26) and was found to have no significant optical activity. Its acidity (cf. Michaelis, *Biochem. Z.*, 1915, **65**, 360) was half that of an albumin preparation but its basicity was about equal to that of the albumin (cf. Euler and Josephson, A., 1923, i, 721). The equivalent concentration of the invertase was found to be $1·64\times10^{-3}$ in 1% solution, corresponding with an invertase equivalent of about 6000; $k_b=3\times10^{-10}$. F. M. H.

Polysaccharides. XXVII. Lichenase. P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, **7**, 916—928; cf. this vol., i, 471).—Lichenase occurs in Plata-barley from the first to the eleventh day of germination. Its amount increases a little after the first day and then remains constant. It is present in nearly constant amount in spinach seeds both before and during germination. During the first few days of germination, the lichenase of maize is distributed equally between the embryo and the endosperm. Subsequently a greater proportion is found in the embryo. Green *Triticum repens* contains lichenase. The enzyme has been found in the intestine of a rabbit (cf. Tschermak, *Biochem. Z.*, 1912, **45**, 452), but all previous attempts failed to reveal it in the alimentary canal of any other vertebrate. It is now shown to be present in the stomach of the pig and of the cow, but not in the rennet-bag of the latter animal. Whether it originates in these places or is introduced along with the food is not certain. Lichenase is not present in the stomach of a calf which has been fed entirely on milk.

The effect of additions on the enzymic hydrolysis of lichenin was studied at p_H 3·94—7·1. Dextrose, lævulose, galactose, maltose, sucrose, cellobiose, and gentiobiose inhibit the action; sodium chloride is inactive; the effect of egg-albumin varies with p_H, but is greatest in feebly acid solution.

Snail-lichenase after dialysis for many days contains no enzymes acting on starch, inulin, maltose, lactose, β-methylglucoside, or ethyl β-methylglucosidosalicylate, and invertase is present only in traces. On the other hand, the enzyme decomposes not only lichenin, but also cellobiose and gentiobiose. The decomposition of gentiobiose supports the theory that cellulose contains glucose residues attached by 1 : 6-glucosidic linkings. W. E. E.

Diastatic Power of the Juice of Different Varieties of Potatoes. A. Joszt and B. Starczewski (*Rozpraw bjolog. z zakresu rolnictwa, hodowli i med. wet.*, 1922; from *Chem. Zentr.*, 1924, i, 2784).—Removal of nitrogenous substances from the juice of potatoes is not completely effected by heating, or by treatment with lead acetate, animal charcoal, or colloidal ferric hydroxide. To accomplish this it is necessary to add 1% ammonium sulphate after heating the juice for 10 minutes at 100°. Considerable differences are shown in diastatic power, but no marked relationship was found between the acidity of the juice, the starch concentration, and the degree of germination. G. W. R.

Influence of Hydrogen-ion Concentration on the Action of certain Amylases. J. T. Groll (*Arch. Néerland. Physiol.*, 1924, 9, 520—538).—Differentiation between various amylase preparations has been studied by comparing the types of curves obtained by plotting the time of hydrolysis of starch against the p_H of the buffered medium (methods are those of the author; cf. *ibid.*, 1918, 2, 516; 1922, **6**, 445). The amylase of ox-blood acts best in an alkaline medium, p_H 8. The amylases of different organs or secretions of the same animal may vary considerably (in man, that of saliva and pancreas; cow, that of milk, blood, and pancreas), or be nearly the same (in man, pancreas and urine). In the same organs of different animals, a similar variation is found; *e.g.*, the amylase of human pancreas differs considerably from those of ox and pig pancreas which are very similar. H. J. C.

Allelocatalysis and the Growth of Yeast. G. L. Peskett (*Biochem. J.*, 1924, **18**, 866—871).—Living yeast-cells grown in bacteria-free media in hanging-drop preparations, multiply in proportion to the number of cells present. The phenomenon of "allelocatalysis," *i.e.*, the mutual acceleration of reproductive rate by contiguous organisms, observed by Robertson (*ibid.*, 1921, **15**, 612) in the case of certain infusoria does not hold true in this case. S. S. Z.

Cannizzaro's Reaction in the Mechanism of Alcoholic Fermentation. C. Schweizer and H. Geilinger (*Bull. Assoc. Chim. Sucr.*, 1924, **42**, 20—31).—The acetic acid and alcohol produced by the action of pressed yeast on acetaldehyde are formed in equivalent amounts, as required by Cannizzaro's reaction, only when oxygen is completely excluded from the reaction mixture. E. S.

Specific Action of Plant Proteases. A. V. BLAGOVESCHENSKI (*Biochem. J.*, 1924, **18**, 795—799).—From experiments on the proteases of *Cannabis sativa*, *Phaseolus Mungo*, *Brassica rapa*, *Lupinus luteus*, *Hibiscus esculentus*, and *Dolichos melanophthalmus*, DC. the author concludes that the enzyme from every plant splits its own globulin more actively than the globulins of other plants. S. S. Z.

Behaviour of Dried Enzymes on Exposure to Heat. III. Pancreatic Enzymes. C. ARTOM (*Arch. Farm. sperim. aff.*, 1924, **38**, 105—132).—Both the enzymes in the pancreas of the dog and those in the pancreatic juice itself, when dried at 10—30°, withstand higher temperatures in the dry state than after re-solution in water. This protective effect of drying is, however, considerably less marked in the latter than in the former of the two cases. These results correspond with those previously obtained with intestinal enzymes. T. H. P.

Ammonia Production by Animal Tissues *in vitro*. I. Use of Mixed Tissue Extracts. J. M. LUCK (*Biochem. J.*, 1924, **18**, 814—824).—A series of experiments with mixed and single tissues is described. Free ammonia is liberated from trypsin-digested caseinogen by the liver and kidney, and very slightly by intestinal mucosa. It is considered to be due to deamidation and not to deamination. Urea was formed by preparations of the liver, intestinal mucosa, and kidney. Marked ammonia production was observed in mixtures of gastric mucosa and liver preparations. No appreciable deamination by either gastric mucosa or liver or other single tissue preparation could be demonstrated. Definite deamidation was effected by the liver, gastric mucosa, kidney, intestinal mucosa, and most liver mixtures. The liver and the liver-mixtures synthesise an amide-like substance. No residual amide nitrogen could be found after the action of a gastric mucosa–liver mixture on totally hydrolysed gelatin. S. S. Z.

Ammonia Production by Animal Tissues *in vitro*. II. Demonstration of Urease in the Animal Body. J. M. LUCK (*Biochem. J.*, 1924, **18**, 825—828).—From experiments on a number of animals, it is concluded that the animal body contains urease. The gastric mucosa of the carnivora gave the most active preparations. The distribution of the enzyme in the stomachs of the ruminants is definite. The enzyme is present in the abomasum where peptic digestion takes place. No urease could be found in the gastric mucosa of the rodents. S. S. Z.

Irregularities in Lactic Acid Fermentation. C. RICHET and H. CARDOT (*Ann. Inst. Pasteur*, 1924, **38**, 842—847).—It is shown that the irregularities observed by the authors in lactic acid fermentation in the presence of mercuric chloride as an antiseptic are dependent on the dilution of the inocula, being more marked at dilution 30,000 than at 300, whilst at a dilution of 300,000 the mercury-treated cultures do not ferment (cf. Lumière, A., 1923, i, 353). J. P.

Regularity of Lactic Acid Fermentation. A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, **38**, 848—850).—Polemical in reply to Richet and Cardot (preceding abstract). J. P.

Influence of Media containing Bile on the Chemical Composition of *Bacillus subtilis*. A. BERTHELOT and E. OSSART (*Bull. Soc. Chim. biol.*, 1924, **6**, 770—772).—Cultures of *Bacillus subtilis* grown in media containing bile and afterwards dried, yield on acid hydrolysis a much smaller proportion of reducing substance (dextrose) than do cultures grown in the absence of bile. J. P.

Bacterial Nutrition. II. H. R. WHITEHEAD (*Biochem. J.*, 1924, **18**, 829—832).—When broth is autoclaved some substances necessary for streptococcal growth are destroyed. These substances are contained in the fraction of the broth precipitable by phosphotungstic acid. This fraction alone, however, is not sufficient. Glycine, alanine, leucine, tyrosine, tryptophan, histidine, aspartic and glutamic acids do not remove this deficiency in the same way as does the filtrate after precipitation with phosphotungstic acid. Caseinogen broth was submitted to fractionation by Dakin's butyl alcohol extraction method, and it was found that the fractions soluble in butyl alcohol, in butyl and in ethyl alcohol, and the fraction insoluble in butyl alcohol did not promote streptococcal growth alone. Complete growth was obtained only when all the three fractions were reunited, although partial growth could be obtained with any two fractions. The fraction insoluble in butyl alcohol was active in high concentration. This was most probably due to incomplete extraction. S. S. Z.

Relation between the Chemical Composition of Peptones and Hydrogen Sulphide Production by Bacteria. F. W. TILLEY (*J. Bact.*, 1924, **8**, 287—295).—Commercial peptones contain unoxidised, partly oxidised, and oxidised sulphur compounds. No hydrogen sulphide is liberated by bacteria from the last named, but freely from the others. Hydrogen sulphide is produced from cystine in abundance. CHEMICAL ABSTRACTS.

Fermentation of Salts of Organic Acids as an Aid to the Differentiation of Bacterial Types. H. C. BROWN, J. T. DUNCAN, and T. HENRY (*J. Hygiene*, 1924, **23**, 1—22).—The production of gas and change of reaction produced by bacteria in organic salt media are irregular and cannot be used as criteria for the differentiation of bacterial types. Suitable data can be obtained, however, because the decomposition of the salts of certain organic acids having insoluble lead salts can be demonstrated by adding lead acetate to the media after incubation (only formic of the simple monobasic and dibasic aliphatic acids is readily attacked; monohydroxycarboxylic acids are also stable but tartaric and citric acids are easily decomposed). Using the sodium salts of citric, *d*-, *l*-, and *r*-tartaric, fumaric, and mucic acids, seven different groupings of the common *Salmonella* types have been obtained (the usual sugar reactions give only four). The method has been applied to other groups of bacteria. Citric acid on bacterial decomposition by

B. suipestifer yields acetic and succinic acids and carbon dioxide; a reaction mechanism is suggested. Fumaric acid yields succinic acid. These organic salt fermentations cannot be used to replace the sugar reactions in general use. H. J. C.

Production of Organic Compounds of Sulphur in Bacterial Cultures with Special Reference to Glutathione. J. W. McLeod and J. Gordon (*Biochem. J.*, 1924, **18**, 937—940).—A distinct nitroprusside reaction was observed in 24—48-hour cultures of a number of anaërobes: *Bacillus paratyphosus* B and most allied species, *Cholera vibrio*, *B. typhosus*, *B. pyocyaneus*, and some strains of *B. coli* and *B. proteus*. No such reaction could be detected in cultures of *Staphylococcus*, *Streptococcus*, *Pneumococcus*, *Gonococcus*, *Meningococcus*, *B. influenzæ*, *B. Morax-Axenfeld*, *B. paratyphosus* A, or the dysentery bacilli. The thermostable substance reacting with nitroprusside is oxidised glutathione or some related compound originally present in the medium and reduced by the organisms in the course of their development. S. S. Z.

Selective Bactericidal Action. E. A. Cooper and G. E. Forstner (*Biochem. J.*, 1924, **18**, 941—947).—The chemical germicides, namely those that react with the constituents of protoplasm, have a more powerful action on *Bacillus coli* than on *B. pyocyaneus*. Formaldehyde forms an exception in this respect, attacking both organisms equally. Germicides, on the other hand, such as the aliphatic alcohols, phenol, etc., which exert a physico-chemical action on bacteria are more active towards *B. pyocyaneus* than towards *B. coli*, and their germicidal action in this case resembles that of heat. S. S. Z.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. IV. Growth-inhibiting Effect of Organic Compounds towards Acid-fast Bacilli. V. Mechanism of Growth-inhibiting Effect of Chaulmoogra and Other Vegetable Oils. O. Schöbl (*Philippine J. Sci.*, 1924, **25**, 123—134, 135—150).—IV.—In general, water-soluble organic antiseptics inhibit the growth *in vitro* of *Bacillus tuberculosis*, whereas fat solvents do not. The sodium, copper, and nickel salts of fatty acids are antiseptic; the zinc, strontium, lead, and uranium salts are inactive. The presence in a compound of an aliphatic double bond, a benzene nucleus, one or more phenolic groups, or an alkyl group attached to a benzene nucleus all tend to increase its antiseptic activity. The amino group in aromatic compounds has no influence if it is attached to the benzene ring but greatly increases the activity if it is in the side chain. Terpenes are less active than their related straight-chain compounds.

V.—Although the degree of unsaturation of vegetable oils does not run parallel with their power to inhibit or to promote the growth of acid-fast bacteria, yet complete hydrogenation abolishes their activity. In terms of Ehrlich's theory the author suggests that all the oils which have any effect on the growth of bacteria have a "haptophore" group by virtue of their unsaturation, and that the

nature of their effect depends on whether the rest of the molecule is a " toxophore " as in the case of chaulmoogra oil or a " nutriphore" as in the case of the growth-stimulating oils. The " nutriphore " in the latter case is the glycerol part of the molecule, the fatty acids being without effect. Some evidence was obtained of acquired tolerance on the part of the bacteria towards chaulmoogra oil.

C. R. H.

Extraction and Purification of Insulin. L. BANTI (*Arch. Farm. sperim. aff.*, 1924, **38**, 176—184).—Marked improvement in the yield of insulin obtained from pancreas is attained by addition of a relatively high proportion of acid to the alcohol used for the extraction, and by the employment of a procedure which gives highly concentrated aqueous solutions of insulin without evaporation in a vacuum. [Cf. *B.*, 1924, Dec. 26.] T. H. P.

Duality of Insulin. L. AMBARD, F. SCHMIDT, and M. ARNOVLYEVITCH (*Compt. rend. Soc. Biol.*, 1924, **90**, 790—792; from *Chem. Zentr.*, 1924, i, 2794).—Two insulin hormones are distinguished : one concerned in the oxidation of sugar to carbon dioxide and water, and the other polymerising sugar to glycogen. An equilibrium appears to exist between the two hormones whereby an increase in the one is associated with a decrease in the other.

G. W. R.

Efficiency of Various Sugars and their Derivatives in Relieving the Symptoms caused by Insulin in Mice. P. T. HERRING, J. C. IRVINE, and J. J. R. MACLEOD (*Biochem. J.*, 1924, **18**, 1023—1042).—Complete positive results were obtained with dextrose and mannose. Maltose was also permanently efficacious, but its action was slower. Temporary disappearance of symptoms was obtained with lævulose, galactose, and tetra-acetylfructose. Lactose, 2 : 3 : 5 : 6-tetramethylglucose, 2 : 3 : 5-trimethylglucose, sucrose, α- and β-methylglucosides, tetramethyl-β-methylglucoside, tetramethyl-γ-methylglucoside, glucose-monoacetone, salicin, mannitol, dulcitol, and β-glucosan had no action at all. The relation of chemical structure and some physiological considerations are discussed. S. S. Z.

Concentration–Action Curve of Insulin Preparations, and Anti-Insulin. S. G. DE JONGH (*Biochem. J.*, 1924, **18**, 833—838).—An anti-insulin substance was observed in some Dutch preparations which showed the phenomenon of double convulsant doses and differed in their behaviour in the case of rabbits and of diabetics. The concentration curve of insulin with regard to sugar seems to be a straight line, that of the anti-insulin an adsorption curve. S. S. Z.

Extraction and Properties of an Ovarian Hormone. E. A. DOISY, J. O. RALLS, E. ALLEN, and C. G. JOHNSTON (*J. Biol. Chem.*, 1924, **61**, 711—727).—Fresh liquor folliculi was mixed with alcohol and the solution evaporated to dryness after removal of the proteins; the residue was extracted with alcohol and the solution treated with

acetone to remove phospholipins, this process being repeated several times; finally the dry residue from the alcoholic extracts was taken up in ether. Amounts of the order of a few mg. of the dry residue from this ethereal solution, when injected into ovariectomised rats, were found to induce the full œstrous cycle in these animals. The active substance is soluble in ether, alcohol, chloroform, light petroleum, or acetone, but insoluble in water. It is thermostable and moderately resistant to both acid and alkaline hydrolysis; it is not affected by tryptic digestion. Preparations with similar properties were obtained from placenta and from whole ovaries, but the yield of active substance was much smaller; no active preparations could be made from corpora lutea. C. R. H.

Durability of Vitamin-*A* of Cod-liver Oil. E. Poulsson (*Biochem. J.*, 1924, **18**, 919—920).—A sample of cod-liver oil 23 years old in daily doses of 3—5 mg. promoted growth in rats deficient in vitamin-*A*. S. S. Z.

Stability of the Vitamin-*A* of Cod-liver Oil Towards the Hardening Process. S. S. Zilva (*Biochem. J.*, 1924, **18**, 881—882).—If anaërobic conditions are observed, cod-liver oil can be hardened at a temperature of 150° and deodorised without any appreciable loss in the vitamin-*A* content. S. S. Z.

Investigation of Barley, Malt, and Beer for Vitamins-*B* and -*C*. A. Harden and S. S. Zilva (*Biochem. J.*, 1924, **18**, 1129—1132).—The vitamin-*B* of barley is not affected by the malting process and is frequently present in the finished malt, but is absent from the culms. The antiscorbutic vitamin appears in the steeped grain and is present in the green malt but absent from kilned malt. The beer examined by the authors (India Pale Ale) was free from both vitamins-*B* and -*C*. S. S. Z.

Fractionation of Bios and Comparison of Bios with Vitamins-*B* and -*C*. G. H. W. Lucas (*J. Physical Chem.*, 1924, **28**, 1180—1200).—The bios contained in malt combings and in rice-polishings can be fractionated by precipitation in alcoholic sclution with barium hydroxide into bios I and II, neither of which has by itself any great influence on the rate of reproduction of *Saccharomyces cerevisiæ*, race F, but together enormously increase the crop of yeast. A top yeast is described, however, which is much less dependent on bios than race F. Bios I and II cannot replace the vitamins in preventing polyneuritis in pigeons or scurvy in guinea-pigs or in maintaining the growth of rats. The growth-producing vitamin can be extracted from rice-polishings by treatment with pepsin. The chemical treatment employed in the fractionation of bios destroys the growth-promoting vitamin. M. B. D.

Action of Nitrous Acid on the Antineuritic Substance in Yeast. R. A. Peters (*Biochem. J.*, 1924, **18**, 858—865).—Primary and many secondary amines are not responsible for the antineuritic activity of acid extracts of yeasts, since such extracts retain their activity after being treated with nitrites. Histamine

sometimes cures polyneuritis in pigeons; this confirms Abderhalden's observations. Daily doses of this drug do not, however, delay the onset of the disease. S. S. Z.

Dietetic Value of Barley, Malt, and Malted Liquors as Determined by their Vitamin Content. H. W. Southgate (*Biochem. J.*, 1924, **18**, 769—776).—Barley and malt, tested on rats, have been found to contain water-soluble-*B* in considerable and equal amounts. Malt has also been shown to possess antineuritic properties in the case of pigeons fed on a basal diet free from vitamin-*B*. Beer independent of its yeast content contains vitamin-*B*, but to a much less extent than that the corresponding amount of malt used in its manufacture. Vitamins-*A* and -*C* are not present in appreciable quantities in barley or its derivatives. S. S. Z.

Nutritive Properties of Milk. III. Effectiveness of the *X*-Substance in Preventing Sterility in Rats on Milk Rations High in Fat. H. A. Mattill, J. S. Carman, and M. M. Clayton (*J. Biol. Chem.*, 1924, **61**, 729—740).—Rats of both sexes fail to reproduce on a milk diet of high fat content; the addition of nucleoprotein to such a diet has no effect, but reproductive power is retained if wheat embryo in added to the food; preliminary ethereal extraction of the wheat embryo, however, deprives the latter of its curative power. This observation, together with the fact that addition of green lettuce leaves to the diet will also prevent sterility, indicates that the missing factor is the substance designated "*X*" by Evans (*J. Metabol. Res.*, 1923, **3**, 233). C. R. H.

Extraction and Determination of Lipochromes from Animal and Plant Tissues. K. H. Coward (*Biochem. J.*, 1924, **18**, 1114—1122).—The only quantitative method of extraction is saponification in an atmosphere of nitrogen with aqueous potassium hydroxide of not higher strength than 20%. Cvet's observation on the existence of four xanthophylls has been confirmed by employing his chromatographic method (fractional filtration of the pigments through a column of chalk). This method has also been found suitable for separating carotin and lycopin from a mixture of the two pigments. A curve for use with the Hellige colorimeter is given for the determination of carotin. S. S. Z.

Lipochromes of Etiolated Wheat Seedlings. K. H. Coward (*Biochem. J.*, 1924, **18**, 1123—1126).—The pigments of etiolated wheat seedlings are carotin and the four xanthophylls isolated by Cvet from green leaves. It is impossible to obtain quantitative figures for the four xanthophylls by Cvet's chromatographic method. S. S. Z.

Yellow Pigments of Australian Acacias. J. M. Petrie (*Biochem. J.*, 1924, **18**, 957—964).—The water-soluble yellow pigment of *Acacia linifolia*, *A. decurrens*, and *A. longifolia* is a glucoside which on hydrolysis yields flavonol, kaempferol, and rhamnose. Free flavonol is absent. The yellow flavonol obtained on hydrolysis

can be transformed by reduction with nascent hydrogen into a red solution resembling that of anthocyanins. The acacia tannins are composed of phloroglucinol and protocatechuic and gallic acids, and deposit on hydrolysis large amounts of the red phlobaphen anhydrides. The flavonol is present in quantities of about 0·06% of the fresh flower, carotin and xanthophyll from 0·14 to 0·3%. S. S. Z.

Grape Pigments. III. Anthocyans of Seibel Grapes. R. J. ANDERSON (*J. Biol. Chem.*, 1924, **61**, 685—694; cf. this vol., i, 1152).—The pigment occurring in the skins of the hybrid Seibel grapes was isolated as the *picrate*, red needles, and converted into the *chloride*, $C_{23}H_{25}O_{12}Cl$, prisms ($+3H_2O$), m. p. 160° (sintering at 158°); on hydrolysis with hydrochloric acid this yields the *anthocyanidin chloride*, $C_{17}H_{15}O_7Cl$, prisms ($+1{\cdot}5H_2O$), m. p. above 260° [*picrate* ($+H_2O$)]. Glucosazone was isolated from the filtrate after the hydrolysis. Methoxyl determinations indicated that the anthocyanidin was a mixture of the mono- and di-methyl ethers of delphinidin, containing a preponderance of the dimethyl ether. Delphinidin iodide was isolated from the solution after removal of the methoxyl groups. Details are given of the absorption spectra of the chlorides of the anthocyanin and anthocyanidin. C. R. H.

Sitosterol. R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 2113—2118).—A sample of sitosterol obtained from the bottom fraction of maize-gluten sterols as previously described (this vol., i, 924) was acetylated and brominated by Windaus and Hauth's method (A., 1907, i, 921). On debromination with zinc dust and acetic acid in alcoholic solution followed by hydrolysis with alcoholic potassium hydroxide, a sitosterol was obtained which on recrystallisation had m. p. 138—139°, $[\alpha]_D^{20}$ —36·69°; acetyl derivative, m. p. 130—131°, $[\alpha]_D^{20}$ —40·20°. Sitosterol from wheat bran and from crude maize oil similarly purified yielded products having m. p. 140—141°, $[\alpha]_D^{20}$ —34·90° (acetyl derivative, m. p. 130—131°), and m. p. 138—139°, $[\alpha]_D^{20}$ —34·87° (acetyl derivative, m. p. 128—130°, $[\alpha]_D^{20}$ —38·81°), respectively, and it is concluded that sitosterol as usually prepared is contaminated with small amounts of dihydrositosterol. The approximate composition of a mixture of the two sterols can be calculated from the formulæ $S=(25{\cdot}82-R)/0{\cdot}6246$ and $P=(36{\cdot}64+R)/0{\cdot}6246$, where S and P represent the percentages of sitosterol and dihydrositosterol respectively, and R is the specific rotation of the mixture in chloroform, the values —36·64° and +25·82° being chosen for the specific rotations of the respective pure sterols. R. B.

Non-volatile Acids of the Peach. E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2337—2338).—Fractionation by the ester-hydrazide method shows that the non-volatile acids of the peach consist chiefly of *l*-malic acid and citric acid in approximately equal proportions. The m. p. 145° is recorded for citric acid trihydrazide (cf. Curtius, A., 1917, i, 635; Franzen and Helwert, A., 1923, i, 637). R. B.

Non-volatile Acids of the Dried Apricot. E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2506—2507; cf. preceding abstract).—The non-volatile acids of the dried apricot, identified by esterification, fractionation, and conversion into the hydrazides, consist of *l*-malic and citric acids in the proportion 2·5 : 1, with traces of an unidentified acid, possibly oxalic acid. F. G. W.

Acetaldehyde : A Normal Constituent of the Tannin-rich Contents of the " Inclusion " Cells in the Mesocarp of certain Fruits. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 218—220).—In a previous paper (this vol., ii, 791) the presence of small amounts of acetaldehyde was demonstrated in certain fruits. The so-called inclusion cells (A., 1919, i, 427) were found to contain acetaldehyde readily liberated from the cell by distillation with 2% tartaric acid. The contents of the inclusion cell of *Ceratonia siliqua*, L, separated by mechanical means, gave a considerable amount of acetaldehyde on distillation with water alone, a further yield being obtained by distillation with acid. The acetaldehyde is considered to be responsible for the coagulation and consequent disappearance of the rough taste of the tannins during the process of ripening. G. S. W.

Ripening Process of Bananas. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 211—227).—During the ripening of bananas the tannin-rich cell contents of the latex tubes present in the pith become coagulated and the tannins pass from a soluble to an insoluble condition. Subsequently the latex tubes break down forming the so-called inclusion cells. These cells are found to contain acetaldehyde in an easily liberated condition (cf. preceding abstract). Fruit in which the normal process of ripening has been suppressed by frost is tasteless and odourless, the formation of sugar from starch and the production of amyl acetate having been inhibited; at the same time, the fruit contains tannin in a soluble condition and only traces of acetaldehyde are present. G. S. W.

Wax from *Fagræa*. A. J. ULTÉE (*Bull. Jard. Botan. Buitenzorg*, 1924, **6**, [3], 1—3; from *Chem. Zentr.*, 1924, i, 2882).—The fruits of *Fagræa* have beneath the outer integument a layer of white, glutinous substance from which, by coagulation with alcohol, a white, slightly elastic mass was obtained, containing ash 0·23%, protein 0·22%, caoutchouc 5·16%. From the first alcoholic extract crystals, m. p. 79°, were obtained which yielded on hydrolysis lupeol, m. p. 211°, and palmitic acid. Phytosterol was also present. G. W. R.

Isolation of an Inhibitory Substance from Plants. W. L. MALLMANN and C. HEMSTREET (*J. Agric. Res.*, 1924, **28**, 599—602).—A substance which inhibits the activity of the cabbage-rot organism was isolated from rotted cabbage plants. The substance was effective against other " soft-rot " organisms, and gave positive results at exceptionally great dilution. It was destroyed by

exposure to a temperature of 63° for 30 minutes, but survived after 20 minutes at 56°. It is not considered to be a product of the soft-rot organism. A. G. P.

Action of Bromine on certain Plants. A. PITINI (*Arch. Farm. sperim. aff.*, 1924, **38**, 164—168).—Decomposition of glucosides contained in plants by the action of bromine (cf. Liotta, A., 1920, i, 587) is the result of a hydrolytic process and takes place either not at all or only partly if the plants are first thoroughly dried. Alkaloids contained in plants are unaffected by bromine only if they are stable towards the halogen hydracid which is formed. T. H. P.

Absorption of Carbon Dioxide the First Step in Photosynthesis. H. A. SPOEHR and J. M. MCGEE (*Science*, 1924, **59**, 513—514).—Dried and ground leaf material, to which the same amount of water has been added as was originally contained in the leaves, absorbs carbon dioxide from the air in the dark; the manner of drying the leaves, however, greatly affects their absorptive capacity. *Helianthus* leaves, similarly treated and free from carbon dioxide, absorbed 4·59 mg. of the latter per g. at 25°. Extraction of the dried leaves with cold absolute alcohol greatly, and with water somewhat, reduced the absorptive capacity, but the material extracted by the alcohol absorbed only very small amounts of carbon dioxide. The absorptive capacity of the leaf is also destroyed by heat. Extraction with acetone did not affect the absorptive capacity, but the latter was reduced by 90% by extraction with water saturated with ether at 20° (Chibnall and Schryver's method for protein extraction), the residue absorbing as much carbon dioxide as the original leaf material. It is considered that support is accorded to the theory that the leaf absorbs carbon dioxide from the atmosphere by a mechanism similar to that which in the blood of mammals serves to free the tissues from this gas. The major portion of the carbon dioxide is probably absorbed by the proteins of the leaf; this primary union may be of importance in determining the cause of the asymmetric nature of the synthesis of carbohydrates in the chlorophyllous plant. A. A. E.

Water Content, a Factor in Photosynthesis. R. H. DASTUR (*Ann. Bot.*, 1924, **38**, 779—788).—Inadequate water-supply results in a decline in the photosynthetic activity of leaves and ultimately causes their decay. This factor also accounts for the fact that Willstätter and Stoll were unable to obtain constant values for the assimilation numbers of the leaves of the same species. O. O.

Chemonastia of *Drosera rotundifolia*. I. W. MEVIUS (*Biochem. Z.*, 1924, **148**, 548—565).—Solutions of the sodium halides cause inflection of the leaf tentacles of *Drosera rotundifolia*, the duration of which varies with the concentration of the stimulating solution, whilst weak solutions produce a quicker response than concentrated solutions. Sodium nitrate is a more active stimulant, but is also more injurious to the leaves than the halides, whilst sodium sulphate only excites the tentacles in concentrated

solutions. Potassium salts show somewhat parallel results, but here the more concentrated solutions act more quickly. The activity of the anions follows the series: $NO_3 > I > Br > Cl > SO_4$. The alkaline-earth chlorides warmed at 51° inhibit the inflection of the tentacles, a similar result being obtained with warm 0·25*N*-potassium chloride solution. A chemical stimulus and a heat stimulus do not summate. *Drosera* leaves kept in a strong solution of alkaline-earth salt and then placed in sodium chloride show an immediate infolding of the tentacles. The alkaline-earth salts exert no harmful action on the leaves. J. P.

Nitrate-reducing Properties of Plants. V. L. ANDERSON (*Ann. Bot.*, 1924, **38**, 699—706).—Nitrate is frequently found in green plants. Of the plants examined more than 20% contained nitrite. The nitrate-reducing mechanism "atite" (cf. Haas and Hill, this vol., i, 349) was observed in 23 plants. Atite does not appear to be of much significance in the protein metabolism of the plant. O. O.

Influence of Nitrifying Bacteria on the Growth of Barley. E. B. FRED (*Soil Sci.*, 1924, **18**, 323—329).—The yield of barley (total dry weight), grown under sterile conditions in sand supplied with nutrient salts and nitrogen as ammonium sulphate, was nearly doubled when pure cultures of nitrifying bacteria were added 2 weeks before planting. The favourable effect on the plants was evident throughout growth, and the presence of nitrates in the inoculated pots and their absence from the others was confirmed by test. The barley contained 0·78% of nitrogen when nitrifying organisms were present and 0·66% in their absence. C. T. G.

Relation of the Molecular Proportions in the Nutrient Solution to the Growth of Wheat. M. C. SEWELL (*J. Agric. Res.*, 1924, **28**, 387—393).—Wheat plants were grown in sand cultures with nutrient solutions containing varying proportions of dissolved salts. Grain yields were as good from solutions high in nitrogen and low in potassium and phosphate as from those with less nitrogen but higher proportions of phosphate and potassium salts. A. G. P.

Antagonism of Hydrogen Ions and Neutral Salt Ions in their Action on the Germination and Growth of Wheat. H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **149**, 207—215).—Calcium and potassium chlorides and sodium dihydrogen phosphate diminish the toxic effect of increasing hydrogen-ion concentrations on the growth of wheat seedlings, more especially between p_H 4·5 and 6·8. The antagonism between salt and hydrogen ions is also shown in their action on germinating wheat seeds. J. P.

Nitrogenous Constituents of the Juice of the Alfalfa Plant [Lucerne]. II. Basic Nitrogen. H. B. VICKERY (*J. Biol. Chem.*, 1924, **61**, 117—127; cf. this vol., i, 1275).—In addition to the asparagine and tyrosine already reported, there have been isolated, from the unhydrolysed juice of the lucerne plant, arginine,

lysine, stachydrine, choline, a purine in the form of its chloride, and a base (unidentified) which gives a picrate melting at 298°. Taken together, the substances so far isolated account for 4·8% of the organic solids and 13·6% of the total nitrogen of the protein-free solution obtained by treating the original juice with alcohol. C. R. H.

Variation with Temperature of the "Swelling Value" of Amylogen. A. MAIGE (*Compt. rend. Soc. Biol.*, 1924, **90**, 685—687; from *Chem. Zentr.*, 1924, i, 2784—2785).—In experiments with the embryos of germinating beans, the critical concentration of sugar at which starch is transformed into amyloplasts was found to be increased both by raising and by lowering the temperature. G. W. R.

Methylpentosans in Cereals. G. TESTONI.—(See ii, 790.)

Determination of Nitrate and Ammonia in Nitrogenous Materials. O. M. SHEDD (*J. Agric. Res.*, 1924, **28**, 527—539).—The Devarda alloy method of Strowd (*Soil Sci.*, 1920, **10**, 333) is modified by allowing the reduction to take place at ordinary temperatures for 24 hours previous to heating. A control experiment on a portion of the test-liquid without Devarda's alloy is carried out with each determination. The method was used for determining nitrate in tobacco leaves and is suitable for the examination of fertilisers. Where nitrate and ammonia are to be determined in portions of the same solution a preliminary filtration is advised. A. G. P.

Determination of Ammonia in Soil. N. BENGTSSON (*Soil Sci.*, 1924, **18**, 255—278).—By successive extractions of soil with potassium chloride solution (25 g. of soil extracted with, at the most, seven 100 c.c. portions of approximately 4% solution), added ammonia could be recovered quantitatively and determined in the combined filtrates. Very low figures were obtained by this method for the ammonia present in air-dried arable soils, indicating that organic nitrogen compounds are not decomposed. A detailed procedure is given (cf. *B.*, 1924, Dec. 26) which proved entirely satisfactory with all surface soils, but failed in the case of one heavy clay subsoil. C. T. G.

Methods of Studying the Strength of Soil Acids. J. W. TIDMORE and F. W. PARKER (*Soil Sci.*, 1924, **18**, 331—338).—A comparison of the strength (intensity factor) of the soil acids in 25 soils, as determined by the Truog "avidity" method (cf. A., 1916, ii, 404), by the sugar inversion method (cf. Rice and Osugi, A., 1918, i, 520), and by the hydrogen-ion concentration showed good correlation between the results. The methods are based on different principles, and the close agreement between the results obtained may be explained by assuming that the acids of the solid phase undergo hydrolysis producing hydrogen ions, the extent of such hydrolysis depending on the strength of the acids. It is considered that the results support the view that the p_H of the soil solution is largely determined by the acid silicates of the soil. [Cf. *B.*, 1924, Dec. 26.] C. T. G.

Influence of Sulphur Oxidation on Solubility of Soil Minerals. R. E. STEPHENSON and W. L. POWERS (*Soil Sci.*, 1924, **18**, 317—321).—The application of various amounts of sulphur to soil maintained at optimum moisture content greatly increased the water-soluble calcium and potassium and decreased the water-soluble phosphorus. Nitrification was depressed by the heaviest application and there was an appreciable increase in acidity. Two soils were used, one representative of arid conditions, with p_H 7·0, and the other of humid conditions, with p_H 6·4. Flocculation of the colloidal material of the soils by the products of oxidation of the sulphur was very marked. It is suggested that the increase in the soluble calcium may account to some extent for the response given by leguminous crops, especially lucerne, to light dressings of sulphur on certain soils. C. T. G.

Absorption of Bases by Soils. N. M. COMBER and S. J. SAINT (*Soil Sci.*, 1924, **18**, 131—132).—Jones (this vol., i, 820) claims to have shown that beyond a certain point an increase in concentration of a base in solution results in a decrease in the amount absorbed by a soil in contact with the solution. This conclusion is based on determinations of the carbon dioxide evolved on shaking carbonates and hydrogen carbonates of alkali and alkaline-earth metals with soil. In the experiments with normal carbonates, the carbon dioxide given off will form hydrogen carbonate with the remaining carbonate and hence cannot be taken as a measure of the amount of base absorbed. Experiments in which the amount of base absorbed by a soil is calculated both from the carbon dioxide evolved and by titration after filtering show definitely that Jones' conclusions are not justified. C. T. G.

Resistance of Soils to Acidification. A. DEMOLON and V. DUPONT (*Compt. rend.*, 1924, **179**, 300—302).—Aqueous extracts of soils from various sources, from which calcium carbonate has been excluded, behave towards both sulphuric and lactic acids as weak buffer solutions. This property is attributed to the humates present. When the soil remains in contact with the aqueous extract, the colloidal clay reacts with sulphuric acid so that the suspension exhibits marked buffer action. H. J. E.

Microscopical Study of Soil. S. WINOGRADSKY (*Compt. rend.*, 1924, **179**, 367—371).—A method of soil treatment is described which yields five specimens for examination from each sample. These are stained with erythrosin. From observation of a series of such specimens the following general conclusions are drawn. Normal arable soil contains only cocci in groups; these are surrounded by a gel or membrane and firmly attached to the particles resulting from flocculation of colloid matter. Mineral débris, except in so far as it is colloidal, is free from microbes; this applies particularly to the coarser particles. In the case of soils to which soluble fermentable matter has recently been added, free microbes, distributed in irregular clusters, predominate. These often consist of forms which are not present in normal soil and are not associated

with colloidal particles. A soil which is foul may readily be recognised by the bacterial forms present in the solution even after centrifuging. [Cf. *B.*, 1924, Dec. 26.] H. J. E.

Secular and Seasonal Changes in the Soil Solution. J. S. BURD and J. C. MARTIN (*Soil Sci.*, 1924, **18**, 151—167).—The concentration and composition of the soil solutions, obtained by the displacement method, from seven soils have been compared, portions of each soil having been kept for 8 years under different conditions, namely, cropped, fallowed, and air-dried. The displaced solution is taken as a trustworthy measure of the true soil solution (cf. *J. Agric. Sci.*, 1923, **13**, 265) and it is assumed that the air-dried soils have remained unchanged and represent the condition of the soils at the beginning of the 8-year period. The cropped soils all showed a marked decrease in concentration of total solutes and nitrates in the displaced solutions at the end of the period, whilst the fallowed soils, with one exception (a highly productive soil), gave considerably increased concentrations. The concentration of phosphate in the cropped soils is decreased—an unexpected result, since it is known that phosphate tends to form a saturated solution and re-establish equilibrium very rapidly. The concentration of sulpha increased in both cropped and fallowed soils.

With soils in a low state of fertility due to continuous cropping, there is a seasonal decrease in concentration of most of the solutes, but the initial concentration of the soil solution in any given growing season returns to its original magnitude by the beginning of the following season. The results cannot be taken to apply to natural drained soils in which the effect of leaching comes into play, since the experimental soils were kept in vessels allowing no escape of drainage water. C. T. G.